MICROWAVE REMEDIATION OF ELECTRONIC CIRCUITRY WASTE AND THE RESULTING GASEOUS EMISSIONS

By

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by

Rebecca L. Schulz

DEDICATION

I dedicate this dissertation to my family and friends, I could not and would not have done it without your love and support.

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Abstract of Dissertation Presented to the Graduate School
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MICROWAVE REMEDIATION OF ELECTRONIC CIRCUITRY
WASTE AND THE RESULTING GASEOUS EMISSIONS

By

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The global community has become increasingly dependent on computer and electronic technology. As a result, society is faced with an increasing amount of obsolete equipment and electronic circuitry waste. Electronic waste is generally disposed of in landfills. While convenient, this action causes a substantial loss of finite resources and poses an environmental threat as the circuit board components breakdown and are exposed to the elements. Hazardous compounds such as lead, mercury and cadmium may leach from the circuitry and find their way into the groundwater supply.

For this dissertation, a microwave waste remediation system was developed. The system was designed to remove the organic components from a wide variety of electronic circuitry. Upon additional heating of the resulting ash material in an industrial microwave,

a glass and metal product can be recovered. Analysis of the metal reveals the presence of precious metals (gold, silver) that can be sold to provide a return on investment.

Gaseous organic compounds that were generated as a result of organic removal were treated in a microwave off gas system that effectively reduced the concentration of the products emitted by several orders of magnitude, and in some cases completely destroying the waste gas. Upon further heating in an industrial microwave, a glass and metal product were recovered.

In order to better understand the effects of processing parameters on the efficiency of the off-gas system, a parametric study was developed. The study tested the microwave system at 3 flow rates (10,30, and 50 ft^3/min) and three temperatures (400, 700 and 1000°C). In order to test the effects of microwave energy, the experiments were repeated using a conventional furnace.

While microwave energy is widely used, the mechanisms of interaction with materials is not well understood. In an effort to better understand how microwaves couple with materials, a newly developed molecular orbital model was investigated. The model proposed an interaction mechanism associated with the development of coupled oscillators upon application of microwave energy. The model was used to model several of the waste gases that appear in the waste stream. Results from experimentation support the data generated thus far.

CHAPTER 1
INTRODUCTION

Microwave energy has been studied by many researchers for waste remediation applications. The reasons for using microwave energy vary depending on the application, but in general, microwave energy is selected because of its unique heating mechanisms, the speed with which samples can be processed, the flexibility of the equipment, and potential energy savings. As many of the waste remediation applications involve heating waste either for the purposes of volume reduction, encapsulation of hazardous components within a glass or ceramic matrix, dewatering, or disinfection, it is reasonable to expect the evolution of some type of emissions from the waste material. The primary waste form discussed in this dissertation, printed circuit boards (CBs), evolves organic and aromatic compounds during treatment, some of which could be hazardous to the population if released to the environment (depending on concentration and exposure level) [CFR90]. Several attempts were made to overcome this problem. Initial experiments on the scrap circuit board material were carried out with a system that used a vacuum pump to evacuate the combustion chamber and then passed the emissions through a liquid nitrogen cold finger to condense the gases [Sch93a, Sch93b]. While this system prevented release of the hazardous emissions to the atmosphere, it did not treat the emissions and created a liquid waste stream that would also require remediation. As microwave energy was being used to process the circuit board material, it

was speculated that microwave energy could also be used to treat the gaseous waste stream simultaneously. A review of relevant literature provided the necessary background information to aid in the design of the system and was also used to assist in selecting the necessary materials and processing temperatures to effectively destroy or decompose the suspected components in the off-gas stream. A tandem microwave waste treatment system was constructed and tested with satisfactory results. However, as is the case with many new designs, it became apparent that many improvements could be made to the system to increase its efficiency. Therefore, a second system with some of the desired modifications incorporated into the design was constructed and tested. Preliminary results from gas chromatography-mass spectroscopy (GCMS) data showed that both microwave off-gas treatment systems appeared to be effective in reducing the concentration and total number of hazardous emissions [Sch95, Sch96, Wic95, Wic97]. Because the initial data were promising, research continued in this area and is the main subject of this dissertation.

Problem Statement

Electronic circuitry is found in every facet of our society. Almost every piece of equipment operated in homes and businesses contains an electronic component. When the item is no longer of use, valuable resources, as well as potentially hazardous materials become a part of the landfill system. This represents a waste stream of many thousands of tons on a yearly basis and a significant loss of finite resources [Lip93, Fis92, EPA89]. In addition, circuitry from defense applications often contains sensitive components that must be disposed of in a secure manner. Circuitry from both waste streams --public and defense-- can be managed effectively using microwave energy. Destruction of sensitive components

is accomplished during ashing (a process which results in a significant volume reduction). Hazardous materials can be isolated in a glass matrix and precious and nonprecious metals can be recovered. Gaseous emissions generated during ashing can be treated simultaneously using microwave energy as well.

Microwave waste remediation studies have been performed on several types of waste circuitry. During the early stages of these studies, it became apparent that a secondary gaseous waste stream was created as a result of the processing regime. In an effort to circumvent this problem, a microwave off-gas treatment system was developed to remediate the emissions as they evolved. Preliminary analyses suggested that microwave treatment was successful in reducing the number and concentrations of the organic species, many of which were listed as hazardous releases in the Clean Air Act [CFR90].

The initial objectives of the work with electronic circuitry were to "destroy beyond all recognition" any components presented for treatment, achieve a significant volume reduction to facilitate storage, and encapsulate any remaining materials that may be hazardous to the environment. In accomplishing these objectives, a microwave waste treatment system was developed that included a microwave off-gas system to control release of emissions to the atmosphere. Furthermore, in order to optimize the potential of the microwave waste treatment system and perhaps enhance its commercial viability, a more complete understanding of how and why the microwave off-gas section functions was necessary. Therefore, the initial objectives of this research were expanded to include a methodolgy to determine the most efficient means for treating the emissions that result from

processing scrap electronic circuitry and to determine the effects, if any, of microwave radiation on the gaseous species.

Dissertation Objectives

Preliminary data showed that microwaves, either through thermal or a combination of thermal and microwave radiation, interact with the various components of the electronic circuitry, including the gaseous products that result from the pyrolysis. In order to develop a more comprehensive understanding of the interaction(s), a microwave waste remediation system was developed and a group of experiments with set parameters and objectives were outlined and carried out. The major objectives of this dissertation were as follows:

➢ Develop a microwave waste treatment system that would allow treatment of all waste circuitry presented for destruction.

➢Develop a methodology for using microwave energy to vitrify the ash residue and to recover metal components.

➢ Develop a microwave off-gas system to decompose or destroy emissions that result from treatment of waste circuitry.

➢ Determine the mechanisms and extent of microwave radiation on the waste circuitry and the products of interaction (solids and gases).

➢ Determine if the observed microwave/material interactions can be modeled or predicted based on molecular orbital theory and coupled oscillators.

Dissertation Overview

Chapter 2 provides the reader with background information from the literature on a variety of topics which include; microwave/material interactions for solids and gases, a section on the legal definitions of hazardous materials, how the relevant waste materials are currently being treated using conventional methods, an overview of microwave waste remediation research in general, as well as in areas more closely related to the subject of this dissertation, and conventional off-gas sampling and treatment techniques. Chapter 3 provides information on the materials and procedures used during the course of the study, as well as a detailed description of the design and fabrication of the various microwave waste treatment systems used during the research. A discussion of the various characterization techniques used to analyze the gases, recovered metals and glass product is also found in Chapter 3. A discussion of possible microwave effects and why this topic may be of interest in the current study initiates the topics for discussion in Chapter 4 in addition to a brief discussion on microwave heating theory. Chapter 5 is a compilation of the results obtained from the various studies and provides a discussion as to the relevancy of the results. Chapter 6 summarizes the dissertation and provides a list of the various accomplishments resulting from the research. Chapter 7 provides suggestions for future studies. In addition, theoretical computer modeling work carried out on some of the gaseous species exposed to microwave radiation based on molecular orbital theory is also presented in the Appendix. A reference section and the author's biographical sketch are also included.

CHAPTER 2
BACKGROUND

Legal Definition of and Regulations for Solid/Hazardous Wastes and Air Pollutants

Introduction

Each year society produces many thousands of tons of refuse material [EPA92]. While efforts are put forth by both public and private sectors to reduce the amount of waste material generated, tons of materials that could be recycled are landfilled on a daily basis. As a result of these practices, dwindling natural resources are lost. The US government has attempted to deal with this problem by passing numerous bodies of legislation designed to define and regulate waste materials, and to identify those materials that may pose a threat to public health. Two such regulations are the Resource Conservation and Recovery Act (RCRA) and the Clean Air Act [EPA88, CFR90, Pat94]. In the following sections, a brief synopsis of what legally constitutes a solid or hazardous waste will be provided, along with a review of gases considered to be air pollutants. The final topic in the section will outline some current and new regulations that create the need to continue research into even more effective waste management and air pollution control devices.

Solid/Hazardous Waste Definitions

According to the RCRA legislation, the term "solid waste" is any garbage, refuse, sludge or other discarded material, including solid, liquid, semi-solid, or contained gaseous

material resulting from industrial, commercial, mining, agricultural or community activities (see Figure 2-1). The term "hazardous waste" is also defined as a solid waste, but with further clarifications to include a solid waste or combination of solid wastes that because of their quantity, concentration or physical, chemical or infectious characteristics may cause or significantly contribute to an increase in mortality or serious irreversible or incapacitating illness; or pose a substantial present or potential threat to human health or the environment when improperly treated, stored, transported, or disposed of (Figure 2-2) [Res88, EPA88].

Once a material has been defined as a hazardous waste, it is further categorized by its ignitability, corrosivity, reactivity or toxicity. Listings of specific hazardous wastes can be found in the Code of Federal Regulations (CFR) 40, Section 261. It is important to note that a mixture of a substance defined as a solid waste and a hazardous waste may or may not cause the material to be considered to be a hazardous waste [Res88]. Because of the many exclusions to the law, a great deal of the materials considered by the public to be "hazardous wastes" (i.e., sewage, agricultural run-off, wastes from coal combustion) are not legally defined as such and are covered under different federal, state and/or municipal regulations.

The US government has established a national policy concerning the generation of hazardous wastes which states that ". . . wherever feasible, the generation of hazardous wastes is to be reduced or eliminated as expeditiously as possible. Waste that is nevertheless generated should be treated, stored or disposed of so as to minimize the

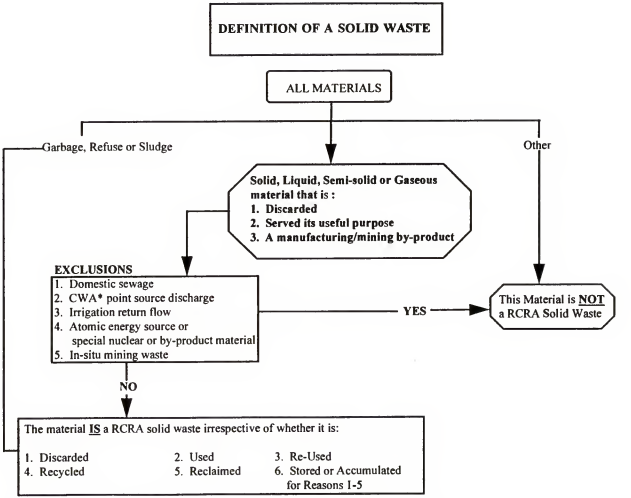

DEFINITION OF A SOLID WASTE
ALL MATERIALS
Garbage, Refuse or Sludge
Other
Solid, Liquid, Semi-solid or Gaseous material that is :
1. Discarded
2. Served its useful purpose
3. A manufacturing/mining by-product
EXCLUSIONS
1. Domestic sewage
2. CWA* point source discharge
3. Irrigation return flow
4. Atomic energy source or special nuclear or by-product material
5. In-situ mining waste
YES
This Material is NOT a RCRA Solid Waste
NO
The material IS a RCRA solid waste irrespective of whether it is:
1. Discarded
2. Used
3. Re-Used
4. Recycled
5. Reclaimed
6. Stored or Accumulated for Reasons 1-5

Figure 2-1. Flowchart defining solid wastes according to the RCRA [Res88]. * CWA = Clean Water Act, as amended.

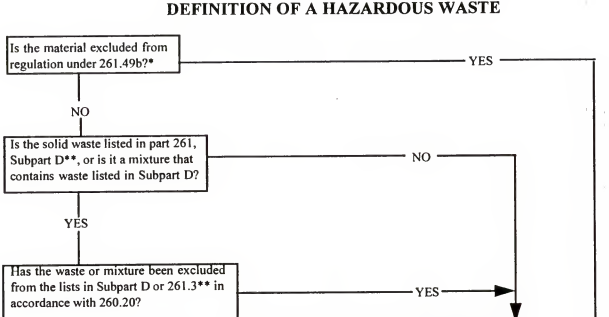

DEFINITION OF A HAZARDOUS WASTE
Is the material excluded from regulation under 261.49b?*
YES
NO
Is the solid waste listed in part 261, Subpart D**, or is it a mixture that contains waste listed in Subpart D?
NO
YES
Has the waste or mixture been excluded from the lists in Subpart D or 261.3** in accordance with 260.20?
YES
NO
Does the waste exhibit any of the characteristics of ignitability, corrosivity, toxicity, reactivity as listed in Part 261, Subpart C?
YES
NO
The waste IS a Hazardous Waste
The waste is subject to control under Subtitle D (if land disposed)

Figure 2-2. Flowchart defining a hazardous waste according to the RCRA [Res88]. * See Figure 2-1 under Exlusions. ** The interested reader is referred to CFR 40, Subpart D, which is a listing of specific hazardous materials and Subpart C - Rulemaking Petitions for Sections 260.20 and 260.22 [Res88, EPA88].

present and future threat to human health and the environment." [USC98]. This policy has caused many businesses, both commercial and defense oriented, to re-evaluate the way their products are manufactured. Some firms are targeting a zero percent discharge, while others have reduced the amount of solid waste transported to landfills by 75-90% [Whi93]. The primary reasons for the reductions are savings to the company in disposal fees, improved public relations and attempting to avoid further federal regulation. The main methods for reduction are source separation (isolating hazardous wastes from non-hazardous wastes), recycling, manufacturing process changes and waste minimization programs (which include substitution of raw materials and/or products) [EPA86]. Due to efforts to dismantle the large stockpile of nuclear weapons, both here and in the former Soviet Union, many tons of electronic circuitry will be available for remediation and recovery operations. Electronic circuitry waste resulting from nuclear weapon dismantlement programs would most likely be exempt from RCRA, but would be subject to the stricter regulations governing nuclear materials [NRC83, EPA85]. However, circuitry from other applications would be considered either a solid or hazardous waste depending on the composition of the board.

Air Pollutants/New Regulations

The first air pollution legislation in the United States was the Air Pollution Control Act passed by the state of California in 1947. This legislation has served as the foundation for many of today's laws governing air pollutants. The law set standards for the discharge of emissions based on set standards, and provided the initial basis for regulation of pollutants

that were determined to be detrimental to human health [Pat94]. The legislation that outlines the current federal government policy regarding air pollutants is the Clean Air Act, as amended, 1990 [CFR90, Pat94]. The amended law listed 189 substances considered to be hazardous air pollutants (Table 2-1). These substances were determined by combining lists of regulated materials from other environmental legislation such as the Emergency Planning and Right-to-Know Act of 1986, the Comprehensive Emergency Response and Compensation Liability Act (CERCLA) and substances regulated by one or more individual states as listed in the EPA's National Air Toxics Information Clearinghouse (NATICH) [Pat94]. When the final list was compiled, many items had been deleted and some were added. It should be noted that only about 33% of the substances on the list have been proven to cause adverse health effects. The remaining substances were listed because of the suspected toxicity associated with exposure. Because of the controversy the bill generated, Congress made provisions for the list to be continually reviewed and revised, as needed. New standards that govern air discharges from municipal waste incinerators were issued in September of 1997. Many incinerators currently in use will have to shut down as they will not be able to meet the new emission standards which require a 76-98% reduction in emissions of air pollutants such as hydrochloric acid, dioxins, furans and toxic metals, such as lead, cadmium and mercury [EPA98].

As will be discussed in later chapters in greater detail, some of the emissions produced during the microwave treatment of the circuit boards are listed as hazardous air pollutants. Because of this, the microwave off-gas system was developed and tested.

Table 2-1. List of Hazardous Air Pollutants Defiined by the Clean Air Act, as amended 1990, Their Structure and Sources [Pat94].

Pollutant	Structure	Sources
Acetaldehyde	Organic	Chemical Industry
Acetamide	Organic	Chemical Industry
Acetonitrile	Organic	Chemical Industry
Acetophenone	Organic	Chemical Industry
2-Acetylaminofluorene	Organic	Chemical Industry
Acrolein	Organic	Chemical Industry
Acrylamide	Organic	Chemical Industry
Acrylic acid	Organic	Chemical Industry
Acrylonitrile	Organic	Chemical Industry
Allyl Chloride	Organic	Chemical Industry
4-Aminobiphenol	Organic	Chemical Industry
Aniline	Organic	Chemical Industry
o-Anisidine	Organic	Chemical Industry
Asbestos	Mineral	Insulation
Benzene	Organic	Chem. Industry, Gasoline
Benzidine	Organic	Chemical Industry
Benzotrochloride	Organic	Chemical Industry
Benyl Chloride	Organic	Chemical Industry
Biphenol	Organic	Chemical Industry
Bis(2-ethylhexyl)phthalate (DEHP)	Organic	Chemical Industry
Bis(chloromethyl ether	Organic	Chemical Industry
Bromoform	Organic	Chemical Industry
1,3-Butadiene	Organic	Chemical Industry, Plastic
Calcium Cyanamide	Organic	Chemical Industry
Caprolactam	Organic	Chemical Industry
Captan	Organic	Pesticide
Carbaryl	Organic	Pesticide
Carbon Disulfide	Organic	Chemical Industry
Carbon Tetrachloride	Organic	Chemical Industry
Carbonyl Sulfide	Organic	Chemical Industry
Catechol	Organic	Chemical Industry
Chloramben	Organic	Pesticide
Chlordane	Organic	Pesticide
Chlorine	Element	Chem. Ind., Disinfectant
Chloroacetic Acid	Organic	Chemical Industry
2-Chloroaceophenone	Organic	Chemical Industry
Chlorobenzene	Organic	Chemical Industry
Chloroprene	Organic	Chem. Industry, Polymers
Cresol/Cresylic Acid (isomers/mixtures)	Organic	Chem. Ind., Coke ovens
o-Cresol	Organic	Chem. Ind., Coke ovens
m-Cresol	Organic	Chem. Ind., Coke ovens
p-Cresol	Organic	Chem. Ind., Coke ovens
Cumene	Organic	Chemical Industry
2,4-D, Salts and Esters	Organic	Herbicide
DDE	Organic	Pesticide
Diazomethane	Organic	Chemical Industry
Dibenzofurans	Organic	Combustion Product

Table 2-1, Continued

Pollutant	Structure	Sources
1,2-Dibromo-3-chloropropane	Organic	Pesticide
Dibuytlphthlate	Organic	Chemical Industry
1,4-Dichlorobenzene	Organic	Chemical Industry
3,3-Dichlorobenzidene	Organic	Chemical Industry
Dichlorethyl Ether	Organic	Chemical Industry
1,3 Dichlorpropene	Organic	Pesticide
Dichlorvos	Organic	Pesticide
Diethanolamine	Organic	Chemical Industry
N-N Diethlaniline	Organic	Chemical Industry
Diethyl Sulfate	Organic	Chemical Industry
3,3-Dimethoxybenzidene	Organic	Chemical Industry
Dimethyl Aminoazobenzene	Organic	Chemical Industry
3,3-Dimethyl Benzidene	Organic	Chemical Industry
Dimethyl Carbamoyl Chloride	Organic	Chemical Industry
Dimethyl Formamide	Organic	Chemical Industry
1,1-Dimethyl Hydrazine	Organic	Chem. Ind., Rocket Fuel
Dimethyl Phthalate	Organic	Chem. Ind., Plasticizer
Dimethyl Sulfate	Organic	Chemical Industry
4,6-Dinitro-o-cresol and salts	Organic	Pesticide
2,4-Dinitrophenol	Organic	Chemical Industry
2,4-Dinitrotoluene	Organic	Chemical Industry
1,4-Dioxane	Organic	Chemical Industry
1,2- Diphenylhydrazine	Organic	Chemical Industry
Epichlorohydrin	Organic	Chemical Industry
1,2 Epoxybutane	Organic	Chem. Ind., Gas Additive
Ethyl Acrylate	Organic	Chemical Industry
Ethyl Benzene	Organic	Chemical Industry
Ethyl Carbamate	Organic	Chemical Industry
Ethyl Chloride	Organic	Chemical Industry
Ethylene Dibromide	Organic	Chemical Industry
Ethylene Dichloride	Organic	Chemical Industry
Ethylene Glycol	Organic	Chemical Ind., Antifreeze
Ethylene Imine	Organic	Chemical Industry
Ethylene Oxide	Organic	Chemical Ind., Sterilizers
Ethylene Thiourea	Organic	Chemical Industry
Ethlidine Dichloride	Organic	Chemical Industry
Formaldehyde	Organic	Chemical Industry
Heptachlor	Organic	Pesticide
Hexachlorobenzene	Organic	Pesticide
Hexachlorobutadiene	Organic	Chemical Industry
Hexachlorocyclopentadiene	Organic	Pesticide
Hexachlorethane	Organic	Chemical Industry
Hexamethylene-1,6 Diisocyanate	Organic	Chemical Industry
Hexamethylphosphoramide	Organic	Chemical Industry
Hexane	Organic	Chemical Ind., Petroleum
Hydrazine	Organic	Chemical Industry, Fuel
Hydrochloric Acid	Inorganic	Chemical Industry
Hydrogen Fluoride	Inorganic	Chemical Industry

Table 2-1, Continued

Pollutant	Structure	Sources
Hydroquinone	Organic	Chemical Industry
Isophorone	Organic	Chemical Ind., Solvent
Lindane	Organic	Chemical Industry
Maleic Anhydride	Organic	Chemical Industry
Methanol	Organic	Chemical Industry, Fuel
Methoxychlor	Organic	Chemical Industry
Methyl Bromide	Organic	Chemical Industry
Methyl Chloride	Organic	Chemical Industry
Methyl Chloroform	Organic	Chemical Ind., Degreaser
Methyl Ethyl Ketone	Organic	Chemical Ind., Solvent
Methyl Hydrazine	Organic	Chemical Industry
Methyl Iodide	Organic	Chemical Industry
Methyl Isobutyl Ketone	Organic	Chemical Ind., Solvent
Methyl Isocyanate	Organic	Chemical Industry
Methyl Methacrylate	Organic	Chemical Industry
Methyl-*t*-Butyl Ether	Organic	Petroleum, Gas Additive
4,4-Methylene bis (2-Chloroaniline)	Organic	Chemical Industry
Methylene Chloride	Organic	Chemical Ind., Solvent
Methylene Diphenyl Diisocyanate (MDI)	Organic	Chemical Industry
4,4'-Methylenedianiline	Organic	Chemical Industry
Napthalene	Organic	Chemical Industry
Nitrobenzene	Organic	Chem. Ind., Coke Ovens
4-Nitrobiphenyl	Organic	Chemical Industry
4-Nitrophenol	Organic	Chemical Industry
2-Nitropropane	Organic	Chemical Industry
N-Nitroso-N-Methylurea	Organic	Chemical Industry
N-Nitrosodimethylamine	Organic	Chemical Industry
N-Nitrosomorpholine	Organic	Chemical Industry
Parathion	Organic	Pesticide
Pentachloronitrobenzene	Organic	Chemical Industry
Pentachlorphenol	Organic	Pesticide
Phenol	Organic	Chemical Industry
p-Phhenylenediamine	Organic	Chemical Industry
Phosgene	Organic	Chemical Industry
Phosphine	Organic	Chemical Industry
Phosphorus	Inorganic	Chemical Industry
Phthalic Anhydride	Organic	Chemical Industry
Polychlorinated Biphenyls	Organic	Dieletrics
1,3-Propane Sultone	Organic	Chemical Industry
B-Propiolactone	Organic	Chemical Industry
Propionaldehyde	Organic	Chemical Industry
Propxur (Baygon)	Organic	Pesticide
Propylene Dichloride	Organic	Chemical Industry
Propylene Oxide	Organic	Chemical Industry
1,2-Propylenimine	Organic	Chemical Industry
Quinoline	Organic	Chemical Industry
Quinone	Organic	Chemical Industry
Styrene	Organic	Chemical Industry

Table 2-1, Continued

Pollutant	Structure	Sources
Styrene Oxide	Organic	Chemical Industry
2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin	Organic	Combustion Product
1,1,2,2-Tetrachlorethane	Organic	Chemical Industry
Tetrachloroethylene	Organic	Chem. Ind., Dry Cleaning
Titanium Tetrachloride	Inorganic	Chemical Industry
Toluene	Organic	Petroleum, Solvent
2,4- Toluene Diamine	Organic	Chemical Industry
2,4-Toluene Diisocyanate	Organic	Chemical Industry
o-Toluidine	Organic	Chemical Industry
Toxaphene (Chlorinate camphene)	Organic	Pesticide
1,2,4-Trichlorobenzene	Organic	Chemical Industry
1,1,2-Trichloroethane	Organic	Chemical Industry
Trichlorethylene	Organic	Chem. Industry, Degreaser
2,4,5-Trichlorophenol	Organic	Herbicide
2,4,6-Trichlorophenol	Organic	Herbicide
Triethylamine	Organic	Chemical Industry
Trifluralin	Organic	Chemical Industry
2,2,4-Trimethylpentane	Organic	Chemical Ind., Petroleum
Vinyl Acetate	Organic	Chemical Industry
Vinyl Bromide	Organic	Chemical Industry
Vinyl Chloride	Organic	Chemical Ind., Polymers
Vinylidene Chloride	Organic	Chemical Ind., Polymers
Xylenes (isomers/mixtures)	Organic	Petroleum, Solvent
o-Xylene	Organic	Petroleum, Solvent
m-Xylene	Organic	Petroleum, Solvent
p-Xylene	Organic	Petroleum, Solvent
Antimony Compounds	Inorganic	Metals, Chemicals
Arsenic Compounds	Inorganic/Organic	Smelting, Chems, Pest.
Beryllium Compounds	Inorganic	Metals, Ceramics
Cadmium Compounds	Inorganic	Chemicals, Smelting
Chromium Compounds	Inorganic	Metals, Plating
Cobalt Compounds	Inorganic	Metals
Coke Oven Emissions	Inorganic/Organic	Coke Ovens, Steel
Cyanide Compounds	Organic	Chemical Industry
Gylcol Ethers	Organic	Chemical Industry, Metals
Lead Compounds	Inorganic	Chemical Industry, Metals
Manganese Compounds	Inorganic	Metals, Chemicals
Mercury	Inorganic/Organic	Chlor-alkali, Biogenic
Fine Mineral Fibers	Inorganic	Insulation
Nickel Compounds	Inorganic	Metals
Polycyclic Organic Compounds	Organic	Combustion
Radionuclides	Inorganic/Organic	Nuclear Industry
Selenium Compounds	Inorganic	Chemical Industry, Metals

However, its efficacy has yet to be tested in an industrial setting. In order to better evaluate the performance of the microwave system, it would be advantageous to determine how conventional off-gas systems treat similar emissions. This topic is discussed in the following section.

Conventional Air Pollution Control/Destruction of Waste Gases

The microwave off-gas apparatus was developed in an attempt to control the release of hazardous air pollutants to the biosphere. However, much work has been done in this area using more conventional or established technologies. Discussions of some of the more prevalent practices for controlling stack emissions along with other means used for the destruction of toxic gases are found in the following sections.

Many companies worldwide have been working toward pollution prevention by changing their processes or the materials used in the their processes in order to reduce or eliminate the need for pollution control devices. Two examples of this include using water-based paints rather than oil-based paints to reduce the amount of hydrocarbon emissions generated by solvents (i.e., paint thinners) and switching from open to closed incineration practices. While preventative methods are generally preferred, they are not always economical or even possible, depending on the nature of the process. As regulations and penalties for failure to comply increase, businesses are continually seeking new and better methods to reduce or eliminate air pollution emissions. Some of these include gravity settling chambers, cyclone separators, electrostatic precipitators, fabric filters, venturi scrubbers, adsorbent and absorbent systems, combustion systems, condensers and hybrid systems that use combinations of the methods listed [Myc95, DeN95]. Many of these devices were

designed to handle particulate emissions (i.e., gravity settling chambers, cyclone, electrostatic precipitators, filters, scrubbers) while others were designed to alleviate problems associated with volatile organic compounds, as well as sulfur and nitrogen oxides (i.e., combustion, condenser and absorbent systems). The thermal systems designed to remediate volatile organics are most closely related to the microwave off-gas system and are described in more detail in the following sections. Several other commonly used types of air pollution control systems are also discussed.

Thermal Incineration/Combustion Systems

Combustion systems are used primarily to control volatile organic compound (VOCs) emissions. Given sufficient temperature and retention time, careful control of combustion and waste flow rate, oxygen availability and the degree of turbulence between the air and combustible materials, most hydrocarbons can be reduced to carbon dioxide and water [Myc95, Pat94]. Thermal incineration can be used to effectively control 80-90% of the 189 substances listed in the Clean Air Act (see Table 2-1) and 75% of the total quantity of toxic air pollutants. The simplified reactions for the oxidation of carbon and hydrogen are shown in the following equations [Myc95, Nev95]:

$$C + O_2 \rightarrow CO_2 + \text{Energy} \qquad 2\text{-}1$$

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Energy} \qquad 2\text{-}2$$

However, in many cases, the emissions are not simple hydrocarbons, but complex organic species which often contain sulfur or halogens. These can produce other pollutants such as sulfur dioxide, acids, phosgene or furans. Incomplete combustion of some types of organic compounds can result in the formation of polychorinated biphenols (PCBs) or

dioxins, both suspected carcinogens [Nie95, Pat94]. Organic emissions and products of incomplete combustion (PICs) have been detected in emissions from a variety of full-scale hazardous and municipal waste incineration processes (incinerators, boilers, and kilns) [Tre87]. The emissions consisted of compounds listed in the Clean Air Act as shown in Table 2-2, along with semi-volatile compounds. In some cases the resulting effluents were believed to pose more of a threat to the environment than the original waste material. Processing conditions within the various waste incinerators consisted of temperatures ranging from 700-1500°C, residence times of 0.2 to 6 seconds and oxygen added to aid combustion in concentrations ranging from 2-15%. The fuel used in most of the tests was natural gas or oil. Some of the kilns used coke or coal as fuel. The authors did not identify the various waste streams, except to state that the waste streams did not contain the specific compounds listed in Table 2-2. Therefore, it was not possible to determine to what extent the emissions were the result of incomplete combustion of the fuels used to burn the waste or incomplete combustion of the waste material itself. As will be seen in the Results section, many of these compounds were detected in the emissions from the electronic circuitry waste.

There are three basic combustion systems that can be used to control gaseous emissions. These are flares, thermal oxidizers and catalytic oxidizers. While each are somewhat similar in design, the operating parameters are significantly different. Determination of which device is best suited to a particular process depends on the concentration of combustible species and contaminants in the waste stream, flow rate, control requirements, and economics.

Table 2-2. Emission Rates of Effluents from Incinerators, Boilers and Kilns. Adapted from Trenholm and Lee [Tre87].

Compound	Incinerator (ng/kJ)■		Boiler (ng/kJ)		Kiln (ng/kJ)	
	Mean	Range	Mean	Range	Mean	Range
Benzene	87	2-980	30	0-300	580	290-1000
Toluene	1.6	1.5-4.1	280	0-1200	nd*	nd
Carbon Tetrachloride	0.8	0.3-1.5	1.8	0-7.2	nd	nd
Chloroform	3.8	0.5-8.4	120	0-1700	nd	nd
Methylene Chloride	2.2	0-9.6	180	0-5800	nd	nd
Trichloroethylene	5.2	2.3-9.1	1.2	0-13	1.3	0.7-2.8
Tetrachloroethylene	0.3	0-1.3	63	0-780	nd	nd
1,1,1 Trichloroethane	0.3	0-1.3	7.5	0-66	2.4**	--
Chlorobenzene	1.2	0-6.0	63	0-1100	152	33-270
Naphthalene	44	0.7-150	0.6	0.3-2.1	nd	nd
Phenol	7.8	0-16	0.3	0-0.8	0.02	0-0.05
Diethylphthalate	3.7	2.8-4.8	0.4	0.04-1.6	nd	nd

■ This emission rate was chosen to normalize results between different facilities taking into account the varying size of the facility and different combustion processes. The rate signifies nanograms of emissions per kilojoule of heat input (ng/kJ).

* = no data
** only one data point

Flares

Flares are usually designed to be smokeless burners. They are classified as either ground-level or elevated, depending on their position within the operation. Elevated flares available are generally selected for safety reasons (removal of the open flame from combustibles and personnel). Flares are used for emergency or intermittent emissions from industrial sources and are also widely used at oil refineries, chemical plants landfill operations and process plants. As the flare is designed to instantaneously combust the waste gases, temperature is the most important parameter to control as there is no residence chamber. The flare tip must be designed in such a manner to allow proper air flow while maintaining flame-holding capabilities. Typical vertical flare devices are shown in Figure 2-3 and Figure 2-4 [Bru96]. In order for the flare to be economical, the waste gas must supply at least 50% of the fuel value to combust the mixture. If the fuel value of the waste gas is less than 50%, then an additional fuel gas is added to the mixture in order to complete combustion [Myc95].

While it may appear that flares offer a simple and inexpensive means of controlling toxic air pollutants, there are several disadvantages to this technology that may make it unacceptable, or require additional engineering to make them practical for use. These disadvantages include excessive radiant heat, luminescence from the flare, noise (mixing at the tip is accomplished using jet venturis), smoke from incomplete combustion, and excessive energy consumption (flame must be constantly maintained and potential energy recovery from waste gases is lost) [Myc95].

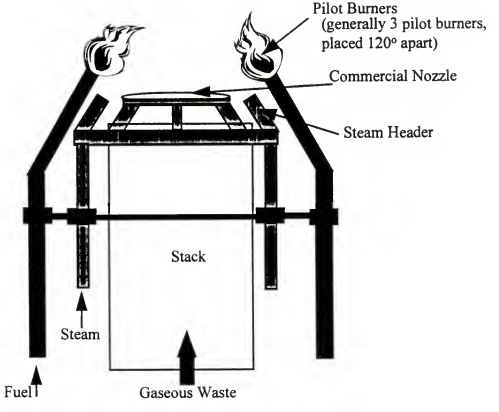


Figure 2-3. Stack flare with mixing nozzle [Bru96].

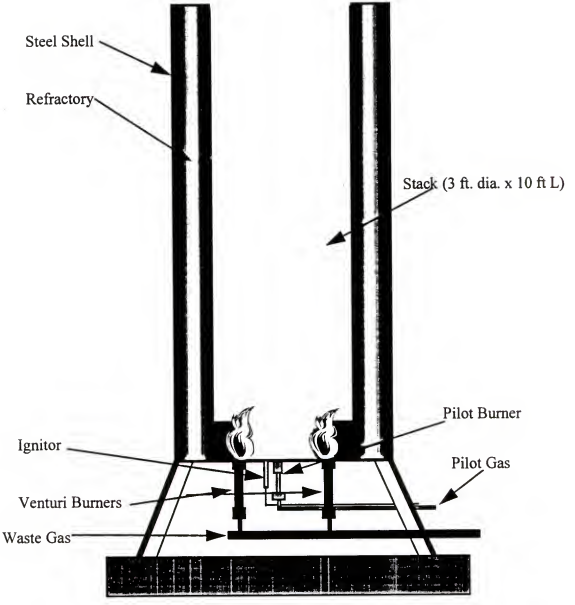


Figure 2-4. Vertical venturi-type flare [Bru96].

Thermal oxidizers

Thermal oxidizers or afterburners are devices that use heat and a residence chamber to decompose gases to carbon dioxide and water. The incineration chamber is lined with refractory materials and is equipped with at least one burner (see Figure 2-5) [Myc95]. The waste gases are passed through the burner and are heated to temperatures in excess of the ignition temperature of the gas. The gases then pass into the residence chamber where they are held for a determined length of time to ensure complete combustion. The residence time is determined by the size of the combustion chamber and is measured after the required temperature has been achieved. As residence time and temperature are dependent on each other, changing either the residence time or temperature requires a corresponding change in temperature or residence time. For example, for a residence time of 0.01 seconds, increasing the temperature from ~650°C to 760°C results in an increase in percent destruction of pollutants from 50% to almost 100%. To achieve the same level of destruction at 650°C, residence time must be increased from 0.01 seconds to approximately 0.1 seconds [Myc95].

Catalytic oxidizers

A catalytic system generally consists of a preheat or burner section where a portion of the waste gas in heated to an appropriate temperature (see Figure 2-6). The remaining portion of the waste gas is mixed with the hot products of combustion prior to passing through the catalytic bed. Temperature is monitored both before and after the waste gas mix passes through the bed to ensure the temperature is sufficient to cause decomposition of the gases and to protect the catalyst material from excessive temperatures. After passing through the bed, the hot gases may be recirculated to a heat recovery system. In a catalytic oxidation

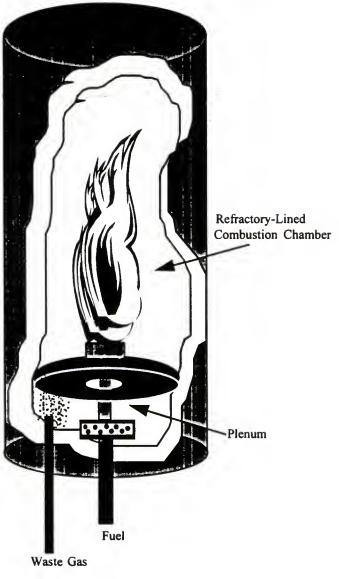


Figure 2-5. Schematic of thermal oxidizer. Adapted from Mycock et al. [Myc95].

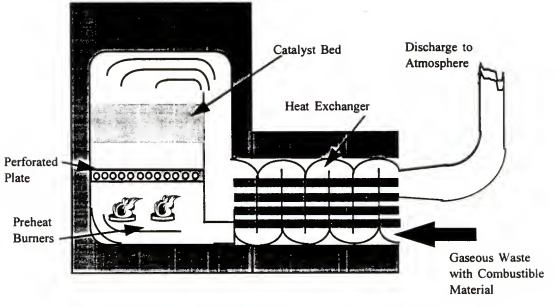


Figure 2-6. Schematic showing a catalytic oxidation system with heat recovery. Adapted from Brunner [Bru96].

process, waste gases are passed through a catalyst bed consisting of a high-surface area ceramic or metallic support material coated with a noble metal such as platinum or palladium. The catalytic bed is designed to allow uniform flow of the waste gas, and to maintain structural integrity of the bed and minimal pressure losses across the surface. The types of bed structures that meet the aforementioned criteria are pellets, honeycomb or mesh matrices. Catalytic incinerators are most often used in systems where the concentration of contaminants in the waste gas are low. The catalyst causes the oxidation reaction to proceed at a faster rate and at reduced temperatures resulting in fuel savings. In air pollution control systems, the oxidation reaction occurs on the surface of the catalyst in the following sequence of events:

- organic compounds in the gas diffuse onto the surface of catalyst
- organic compounds are absorbed onto the surface
- oxidation occurs
- new compounds desorb after reaction occurs (CO_2 and H_2O)
- new compounds diffuse back into the exhaust air stream

There are several challenges associated with a catalytic incinerator. "Poisoning" of the catalyst is one of the main concerns and occurs when certain metallic species combine or alloy with the catalyst rendering it ineffective. The poisons are divided into two categories, fast-acting poisons which include; phosphorus, bismuth, mercury, arsenic and antimony, and slow-acting poisons which include lead, zinc and tin. At temperatures in excess of 1000°F (~538°C), copper and iron are capable of alloying with platinum thereby reducing its effectiveness. Other materials such as sulfur and halogen compounds act has

inhibitors or suppressants in the oxidation process. However, their effect on the catalyst is not permanent; once the compounds are removed, the catalyst can once again function normally. Another problem that occurs within the catalyst bed is referred to as thermal aging. This occurs when the catalyst is exposed to temperatures in excess of 1500°F (~816°C). This can cause rapid deterioration of the catalyst bed material decreasing its reactivity. Other problems that may arise include loss of catalyst material from erosion, attrition and vaporization.

The primary reason for selecting a catalytic incinerator is economics. Because the system operates at lower temperatures, fuel expenses are decreased in some cases by 40-60%. Lower temperatures also permit less costly building construction materials [Myc95, Bru96].

Other Air Pollution Control Systems

Condenser systems

There are two categories of condenser systems. These are contact and surface condensers. Within each category there are several different types of systems available for selection as shown in Figures 2-7 and 2-8.

Contact condensers are generally simple in design and require a liquid coolant such as water to come in direct contact with the air waste stream. The water cools the gases and allows them to condense. However, while perhaps avoiding, or at least decreasing an air pollution problem, a secondary liquid waste stream is often created.

Surface condensers also make use of coolants, but the coolant is separated from the waste stream by a heat transfer surface. Coolants can consist of water, chilled water, brine

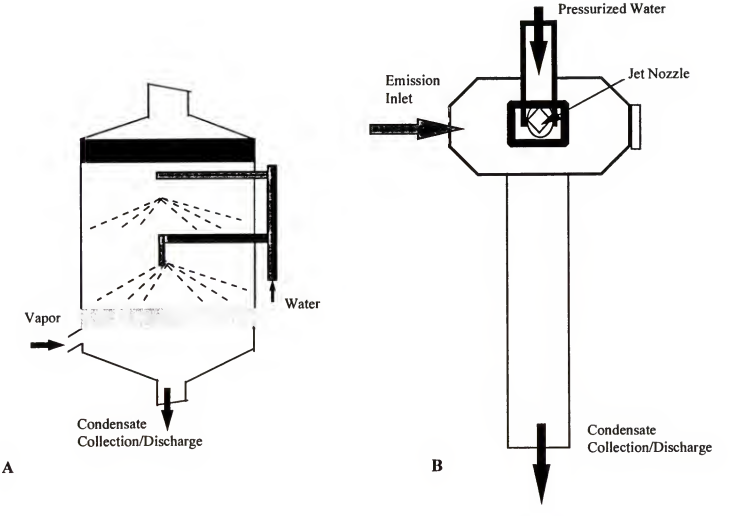


Figure 2-7. A) Spray contact condenser; B) Jet ejector contact condenser. Contact condensers are conventional off-gas systems used to remove waste gases from process systems, but usually create an additional secondary liquid waste stream. Adapted from Mycock, et al. [Myc95].

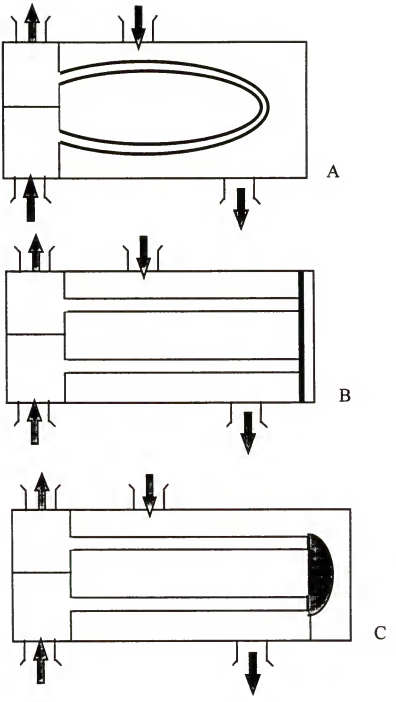


Figure 2-8. Schematics showing examples of shell and tube surface condensers. A) U-tube or hairpin; B) fixed tube; C) floating head. Adapted from Mycock, et al. [Myc95].

solutions and Freon. Air condensers have also been used, but are usually much larger than water condensers due to the low specific heat of air (approximately one-fourth that of water) [Myc95]. This problem can be somewhat circumvented by increasing the surface area of the condensers by adding fins or disks to the outside surface of the heat exchanger tubes. The selection of coolant is based on the degree of cooling required to achieve condensation.

Condensation occurs via the formation of droplets or films. When drops are formed, they fall from the condensate surface leaving the surface free to allow formation of additional droplets. When a film is formed, it coats the condensate surface and additional vapors must condense on the film surface rather than on an exposed metal surface. Since most gases condense in this manner, surface condensers usually consist of a tube design which allows condensation to occur on either surface of the tube. Other materials such as oleic acid on nickel or chrome plate can be used to promote dropwise condensation, as can benzyl mercaptan on copper or aluminum. These substances prevent the metallic surface from being wetted by the condensate.

As with the previous air pollution systems surface condensers also have disadvantages associated with their use. Because condensation requires a large temperature difference between the gases and coolant, large thermal gradients are present in the tube material. These thermal gradients cause the formation of stresses to develop due to expansion and contraction of the tube metal. Because the tubes are physically connected to the outer shell, buckling of the tubes can occur and eventually cause destruction of the condenser. A way to eliminate this problem is to attach one end of the tube bundle to the shell and allow the other end to remain structurally independent allowing the tubes to expand

and contract within the shell. This is referred to as floating head construction. Other factors to take into account prior to selecting condensation as an air pollution control method are volatility, concentration, miscibility and stability of the waste gas components. Methods to improve efficiency can range from simple regular cleaning of the surfaces to increases in pressure, mechanical refrigeration, and other coolants such as liquid nitrogen.

Absorbent/adsorbent systems

In an absorbent system, removal of air pollution emissions is accomplished through the dissolution of the gas molecules in a liquid media (usually water). Absorbers can be used to remove gaseous contaminants as well as particulates. However, the system is usually optimized to handle one or the other. Absorption takes place due to a concentration difference between the absorbent (liquid) and the absorbate (contaminant) and involves a mass transfer rather than a heat transfer. Absorption will continue to occur as long as there is a sufficient concentration gradient between the two media. Critical factors in designing an absorber for gas emissions for optimum mass transfer include a large interfacial contact area, effective mixing of the gas and liquid, sufficient residence time to allow absorption to occur, and selecting the correct liquid media such that absorption can occur [Myc95, DeN95].

There are several different types of absorbent systems including; spray towers, venturi scrubbers, and packed columns or towers. A spray tower is somewhat similar in design to the spray condensate unit. In the spray tower, the nozzles are configured to cover the entire diameter of the tower. In practice spray towers are usually selected for applications where the gas in very soluble in the liquid or in applications where removal

efficiency is not critical. Venturi scrubbers are generally used for particulate removal due to the high velocity of gases through the venturi throat (100-400 ft/s) making it difficult to achieve adequate contact time between the gas and liquid. Packed towers or columns are found in a variety of configurations with many different types of packing media. The packing media is selected such that it allows for the large surface area for continuous liquid/gas contact and particulate entrainment. They are the most widely used absorbent system for gas emissions. In a cross flow packed tower as shown in Figure 2-9, emissions are forced in a horizontal direction through the packed bed. The liquid absorbent filters down through the bed in a vertical pathway. At the same time, horizontal sprays are aimed at the face of the bed. The face of the bed is slanted in the direction of the incoming gases. Gases are absorbed by the liquid and particulates are entrained by the packing material. Absorbate liquid is collected at the bottom of the tower. This type of system, and others with slightly more complex designs can be tailored to remove particulates in one portion of the bed and gas molecules in another. Furthermore, if the bed is partitioned, chemicals can be added to the liquid to target specific gases, as the gas proceeds through the tower, additional sections may be available to permit further purification of the gases prior to release to the atmosphere or a secondary system.

In an adsorbent system, gas molecules adhere to the surface of a material. Materials used as adsorbents are generally very porous and most adsorption takes place on the internal surfaces of the particle through either a chemical or physical adsorption mechanism. The types of materials generally found in adsorption beds are activated carbon, silica gels, molecular sieves, and porous alumina pellets.

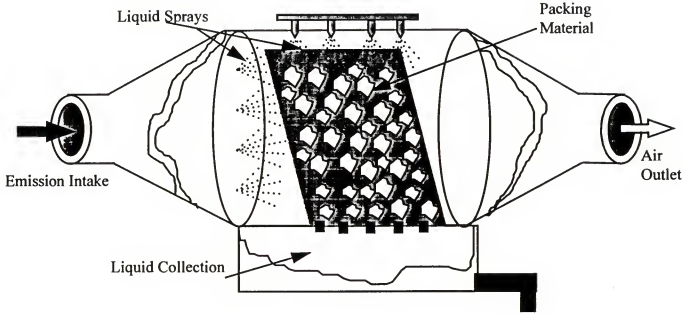


Figure 2-9. Schematic showing the cross flow packed tower absorption system. This is one of the most widely used absorption systems for cleaning waste gases from stacks. Adapted from Mycock, et al. [Myc95].

Adsorbent systems are primarily used for air purification processes when the contamination present is very dilute (< 1ppm). In this situation, thin bed adsorber systems are used. Some examples of this type of technology are filter cartridges in respirators, cigarette filters and home air purification devices. On an industrial level, adsorbent systems are often used for solvent recovery operations where concentration of the vapors must exceed 1000ppm in order for the recovery operation to be economically feasible [Myc95]. An example of a solvent recovery system is shown in Figure 2-10.

Depending on the adsorption mechanism, the bed material can either me cleaned (regenerated) and reused, or must be disposed of and replaced with a new filter bed. Systems that rely on chemisorption (where a chemical bond is formed between the adsorbent and adsorbate) are often difficult or impossible to regenerate and recovery of the adsorbate is not possible. Processes that use a physical adsorption mechanism can usually be regenerated through the use of heat and or steam and recovery of the solvent is relatively simple [DeN95, Myc95, Pat94]. As shown in Figure 2-10, a series of adsorbent containers can be connected to each other in series. While two of the containers are used to remove organic vapors from the air waste stream, the third container is subjected to cleaning and recovery processes. In this automated process, a system of valves moves the contaminated air stream from one adsorbent vessel to the next. When the first container becomes saturated with adsorbate, primary the air flow is shunted to the second container, and gases that are vented from the second container then pass to the third container. The saturated container is subjected to regeneration processes. With this cycling process, two containers are always available for use.

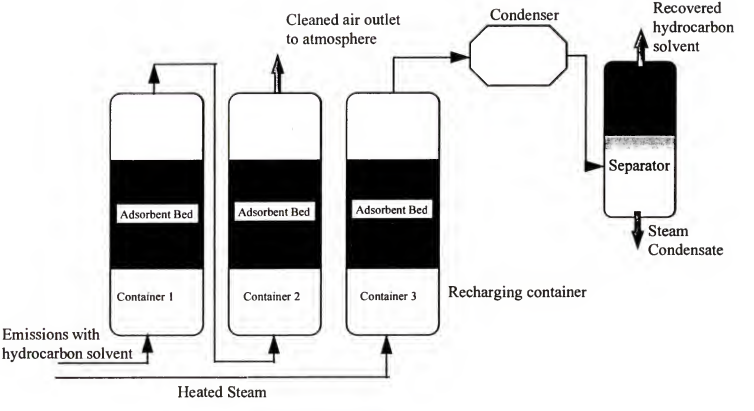


Figure 2-10. Adsorbent system for volatile organic comounds. In this schematic, containers 1 and 2 are active in removal of VOCs while container 3 is shown in recharge. Automated processes allow for continual switching of containers such that 2 are available for adsorption while the third is cleaned and made ready for re-use. Adapted from De Nevers [DeN95].

The above paragraphs serve to illustrate the different types of air pollution control technology that is currently available. In some cases, more than one type of pollution control system is used in conjunction with another system in order to improve the quality of air released to the atmosphere. These are often referred to as hybrid systems. The concentration and nature of the air pollutant to be controlled determines which control devices are employed. Once a control device or hybrid system is selected, continual or periodic testing of the emissions from the process must be collected to determine if the system is functioning properly. Descriptions of EPA accepted methods for air sampling are provided in the following paragraphs.

Standard Gas Sampling Methods

The Environmental Protection Agency under RCRA has established procedures for collecting semi-volatile and volatile organic compounds for determining the efficiency of hazardous waste incinerators. Two methods of interest are Modified Method 5 (MM5) or the semi-volatile organic sampling train used to collect semi-volatile organic species (semi-VOST) and the volatile organic sampling train (VOST) also referred to as Method 0030. Semi-volatile compounds are defined as those with boiling points in excess of 100°C. Many compounds fall into this category and some compounds of interest that can be collected through the MM5 sampling technique include toluene, naphthalene, xylenes and styrene. Method 0030, or the volatile organic sampling train (VOST), is used to collect VOCs with boiling points less that 100°C [Pat94]. Some compounds of interest that can be collected with this method include benzene, chlorobenzene and toluene. In practice, both methods can be used to successfully collect compounds with boiling points ranging from approximately

100°C to 120°C, as evidenced by the mention of collection of toluene for both methods. Simplified schematics of both collection methods are shown in Figures 2-11 and 2-12. In method MM5, a highly porous polymeric resin (trade name XAD-2™) is used to adsorb the semi-volatile organic compounds. Any compounds that may pass through the trap are condensed by the impingers that follow. The filter at the front-end of the sampling train is filled with glass or quartz fibers that collect particulate matter. Analyses are carried out using gas chromatography with mass spectroscopy (GC-MS) and/or high performance liquid chromatography (HPLC).

In Method 0030, as shown in Figure 2-12, the incoming waste gas is cooled by passing through a water-cooled condenser. Once the gas is cooled, VOCs are collected within the sorbent cartridge. There are three traps in the cartridge. The first two contain Tenax™ (a porous polymeric resin) and the third contains charcoal. Liquid condensate is collected in an impinger that is located between the two Tenax traps. The traps are replaced every 20 minutes during a two-hour sampling period providing six sets of traps for analyses. Analysis of the traps is accomplished using GC-MS thermal desorption methods.

There are many other EPA accepted sampling techniques and analytical methods, each targeting a specific group of compounds or metals [Pat94]. No one method has been approved to detect all the products that may be found in a hazardous waste stream. Therefore, more than one method may have to be employed to completely characterize the waste stream.

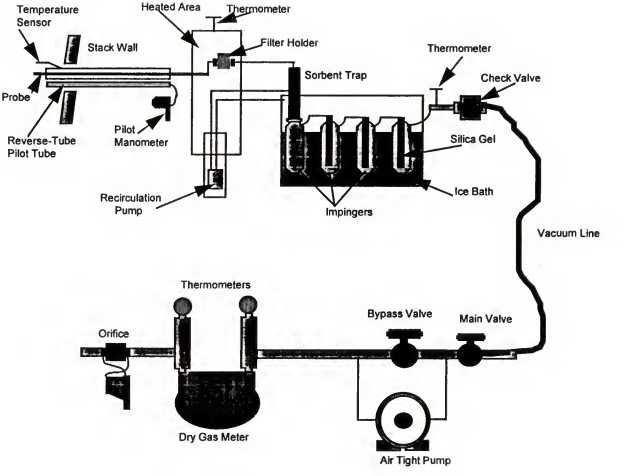


Figure 2-11. Schematic of the RCRA accepted Modified Method 5 (MM5) or semi-VOST sampling train used to collect semi-volatile species for analyses. Adapted from Patrick [Pat94].

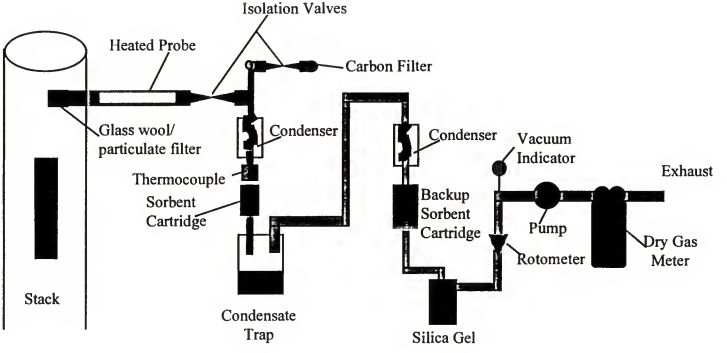


Figure 2-12. Schematic of the RCRA accepted volatile organic sampling train (VOST) used to collect volatile organic species for analyses. Adapted from Patrick [Pat94].

Microwave Energy and Waste Remediation

While microwave technology has been in use for over 40 years, processing waste materials using microwave energy has only recently been recognized as a promising alternative remediation technique. Microwave processing of waste materials may not be appropriate for every situation and is still in the developmental stages for most waste reduction/destruction applications. However, microwave energy offers several advantages over conventional processing methods. These benefits include [Sch93a, Pet93a, Sch94b, Wic95, Cla96]:

- large volume reductions,
- weight reductions,
- leach resistant final product,
- toxicity reduction,
- flexibility in processing a wide variety of waste streams,
- ability to handle several waste streams simultaneously,
- remote and mobile capabilities,
- efficient processing times,
- possible reduced energy expenditures and
- high and low temperature processing within the same system.

However, these advantages do not preclude the challenges often associated with a newly emerging waste remediation processing method. Some of the challenges for developing a turn-key microwave processing method include lack of public acceptance of the technology, reluctance to change current strategies, modifying existing equipment to fit specific needs, heating low-loss materials, temperature measurement and economics.

As the benefits of using microwave energy have been generally thought to exceed any anticipated complications, much study has been carried in this area with many different research projects which have demonstrated the successful use of microwave energy to treat

a variety of wastes [Dau91, Oda91, Dau92, Oda92, Oda93, Sch94b, Wic95]. In the following sections, a brief description of relevant and related microwave waste treatment studies on solid, liquid and gases will be provided.

Microwave Waste Remediation of Solids and Liquids

Microwave energy has been used to treat a variety of both solid and liquid waste forms. Applications related to the studies described in this work, or work done previously by the author using the equipment described in this text, will be discussed in the following section.

Radioactive and simulated radioactive waste

The use of microwave energy for the remediation of a variety radioactive wasteforms has been investigated by several researchers. Allen [All82] and Morrell et al. [Mor86] describe work that was initiated in the United Kingdom in 1975 to vitrify high-level liquid radioactive waste streams. Both authors describe a process whereby fiberglass cylinders were slowly pushed through a stainless steel tube. Liquid waste (both simulated and actual radioactive waste have been tested) was pumped through the tube and allowed to absorb into the fiberglass matrix. The liquid was then rapidly evaporated by microwave energy. Gases arising due to the evaporation process were passed back to a condenser through the advancing fiber glass cylinders. In earlier work [All82], the cylinders were vitrified using conventional heating methods. In Morrell's paper [Mor86], the dried cylinders were passed to a microwave powered melter and subjected to temperatures sufficient to cause vitrification of the cylinders and the formation of a homogeneous waste glass product (see Figure 2-13). The authors further mention that at the end of the study, the equipment was easily

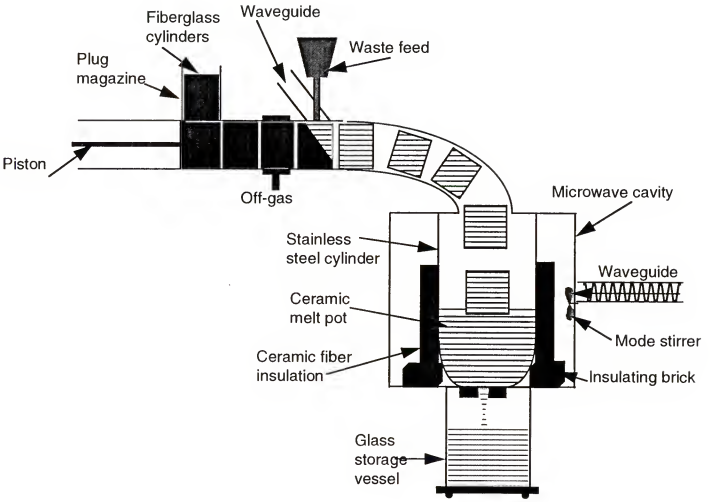


Figure 2-13. Schematic showing the microwave fiberglass vitrification system developed by Morrell, et al. to remediate high-level radioactive waste [Mor86].

decontaminated and returned to service in a non-radioactive laboratory. This clearly illustrates one of the main advantages for using microwave energy in hazardous waste work.

Koizumi et al. [Koi83] described the development of a system to convert plutonium-uranium nitrate solutions to oxide powders using microwave heating. A constant volume of mixed nitrate solution was pumped to a denitration vessel and subjected to microwave heating. The solution was concentrated and denitrated due to vaporization of nitric acid and decomposition of mixed nitrates. A PuO_2-UO_3 oxide cake was formed. Several additional steps were taken using conventional heating methods to obtain the desired PuO_2-UO_2 powder. Because laboratory scale tests were successful, a Plutonium Conversion Development Facility was constructed at the Tokai Reprocessing Plant in 1980, with plans underway to construct a larger scale version of the facility. According to Komatsu [Kom91] this large-scale treatment facility referred to as the Plutonium Contaminated Wates Treatment Facility (PWTF), was put into operation at the Tokai Works of the Power Reactor and Nuclear Fuel Development Corp. in 1988. Operating conditions are described in the following paragraphs.

Komatsu and colleagues [Kom90, Kom91, Ohu90] developed an in-can microwave melter to solidify and condense plutonium contaminated incinerator ashes. The system uses a 0.915 GHz microwave generator with maximum power output of 25kW. Microwaves are launched to the melter via a waveguide. Water is used to cool the microwave generator as well as the melter. Nitrogen is used to prevent oxidation of the stainless steel cannisters. An off-gas treatment system is used to contain dusts and fumes generated during melting operations. Though not fully detailed by the authors, reference is made to an automatic

cleaning system as well as automated controls. Wastes are fed to stainless steel canister (volume = 42 liters) with a continuous screw feeder at a rate of 15kg/hr. One canister can hold approximately 105 kg of the ash material. Maximum operating temperature for the system is approximately 1450°C.

A second system developed by the same authors describes a method for treatment of β, and γ-contaminated ashes. This waste is generated from materials such as gloves, paper, protective clothing, shoes, plastic sheeting and bags from nuclear power plants that has been incinerated to reduce its volume. Once incinerated, the resulting ash is stored in containment drums. Samples of this ash were solidified using a 2.45GHz, 6kW microwave unit and a cylindrical metal crucible. Several fluxes were added to reduce the melting temperature of the ash and to improve the durability of the final wasteform. Samples of the solidified waste were leach tested for periods up to six months in accordance with recognized testing procedures with acceptable results.

This facility uses a microwave energy source operating at 0.915GHz. Microwaves are launched into a water-cooled melter via a waveguide. A nitrogen atmosphere is used to prevent oxidation of the stainless steel crucible and also provides cooling for the crucible.

Researchers at the Rocky Flats site in Colorado have done extensive work on using microwave energy to vitrify several different radioactive and non-radioactive wasteforms, including in-situ solidification of simulated and actual precipitation sludges (generated as a result of plutonium and americium recovery), transuranic (TRU) wastes, incinerator ashes, nitrate salts and contaminated soils [Pet87, Pet91, Pet93, Pet93a, Kra93, Esc94, Dix94, Fen94, Fen95, Spr95, Tha96, Pet97]. A schematic of the Rocky Flats pilot-scale microwave

solidification system is shown in Figure 2-14 [Tha96]. Within a glove-box, a 30 gallon stainless steel drum is placed on a lift and raised until it comes in contact and forms a seal with a lip in the top chamber. An insulation housing equipped with thermocouples is secured around the drum in order to minimize thermal losses and to measure temperature. Temperatures within the drum are measured with an infrared thermometer. Through the top chamber, waste and glass frit which have been mixed, dried (if necessary), and formed into pellets or briquettes are fed into the drum. Microwave energy is then introduced into the drum via a waveguide (microwave generators and other control equipment are placed outside the glove-box area for safer and easier access by personnel). The drum is rotated on a turntable to ensure even distribution of the microwave energy. As the frit/waste mix melts, additional feed is introduced until the drum is filled to capacity. The drum is then transferred to a cooling area. Once cooling is complete, samples of the glass wasteform are taken to ensure the material meets regulatory requirements. Tests conducted include bulk density, specific gravity, moisture content, compressive strength, resistance to weathering (freeze/thaw, wet/dry), permeability, and chemical durability. Once the drum material passes testing procedures, it is sealed and placed in a 55-gallon drum acceptable for transportation and storage. The 55-gallon drum is fitted with a series of Styrofoam spacers and metal rings to ensure proper positioning of the 30-gallon drum and to create a secure seal suitable for transport.

The feasibility of using microwave-induced plasma sintering method for synthetic Idaho Chemical Processing Plant nuclear waste calcines was reported by Park et al [Par91]. The alumina- and zirconia-based high-level nuclear waste ceramics were processed in as

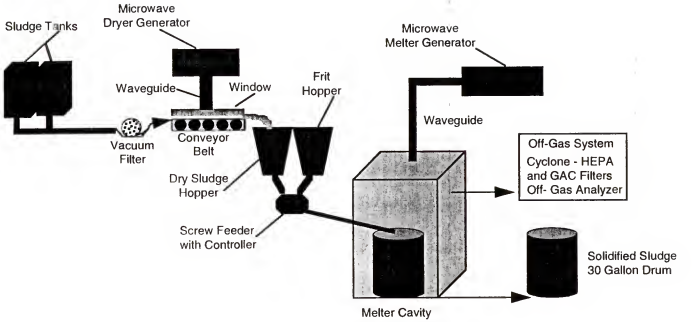


Figure 2-14. Schematic representation of the Rocky Flats microwave vitrification system designed to vitrify radioactive wastes [Tha96].

little as ten minutes with densities > 3.20g/cm^3. Glass frit was added in some tests to lower fusion temperatures. However, this resulted in lower densities, increased evolution of volatiles along with the formation of additional crystalline phases ($Na_3KAl_4Si_4O_6$). Other data gathered on the densification behavior, microstructure and phases formed were also provided.

Jantzen et al. [Jan91] reported using a 2.45GHz, 1000W microwave oven (Model MDS-205, CEM Corp., Matthews, NC) to vitrify simulated nuclear waste slurries, conventional and microwave dried slurries, and the Defense Waste Processing Facility (DWPF) "start-up" frit (SR-165). Jantzen's studies showed that a homogenous glass could be produced in 10-15 minutes at 1150-1200°C. Longer processing times and lower temperatures caused the formation of spinels ($NiFe_2O_4$ spinel, Fe_3O_4 spinel) or crystalline phases ($MgSiO_3$ (enstatite), $2SiO_2{\cdot}3Al_2O_3$ (mullite)). Higher temperatures and shorter times caused significant volatilization of alkali species and recrystallization of the glass. It was also observed that the microwave processed glasses appeared more homogenous than those processed conventionally and that microwave energy could be used to both dry and vitrify the slurries in less time and space. This is advantageous when considering the processing must be carried out in a shielded area and all sample transfer must be done remotely.

Schulz et al. conducted a study to determine the effectiveness of using microwave energy to process simulated high level nuclear waste glass [Sch91, Sch94a,b]. Several different experiments were carried out using a 2.45GHz, 6400W Raytheon RadarLine industrial microwave (Model #QMP-2101B-6), alumina and fused silica crucibles and a susceptor to aid in heating. The experimental setup is shown Figure 2-15. Various tests were

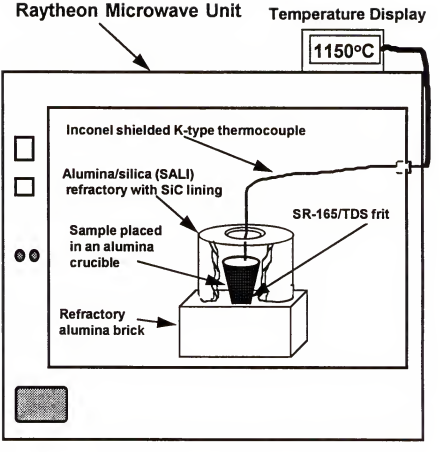


Figure 2-15. Microwave set-up for SR-165/TDS vitrification study. The study was conducted to determine the feasibility of using microwave energy to process high-level radioactive waste.

conducted using a borosilicate glass composition combined with simulated nuclear waste materials (SR-165/TDS) and the basic glass frit (SR-165). The compositions of these glasses are found in Table 2-3. Heating rate experiments showed that the glasses reached a critical temperature (temperature where microwave energy begins to interact with the material) at or near the glass transition temperature, T_g (see Figure 2-16) [Sch94b]. The glass transition temperature is usually defined over a range of temperatures where the glass undergoes a transformation from the glassy state to a supercooled liquid [Kin76]. Dielectric measurements taken on powdered (frit) and core-drilled samples through a range of frequencies showed an increase in tanδ at temperatures near T_g (see Figures 2-17, 2-18). It was speculated that the increases in the dielectric loss factor were due to a combination of conduction, relaxation and deformation loss mechanisms [Sch94b]. These mechanisms depend on the movement of alkali species, network deformation and relaxation times. Therefore, it was expected that lower dielectric losses (and slower heating rates) would occur until the temperature reached T_g where movement of the species through the network would be easier. As temperatures increase, ion oscillations approach that of the electric field and dielectric losses increase. This results in greater electromagnetic to thermal energy conversion which in turn lead to an increase in the temperature of the glass.

Other experiments were conducted to determine the effect of processing or soak time. For this experiment, a mixture of 50% SR-165/TDS and 50%SR-165 was used to determine the processing time necessary to achieve a homogenous melt. Samples were brought to the recognized processing temperature for these glass compositions (1150°C) and held for

Table 2-3. Borosilicate Glass Compositions [Sch91].

Component	SRL-165 (wt%)	SR-165/TDS (wt%)
SiO_2	68.0	54.1
B_2O_3	10.0	6.8
Na_2O	13.0	10.3
MgO	1.0	0.8
ZrO_2	1.0	1.2
Fe_2O_3	--	12.3
Li_2O	--	4.7
MnO_2	--	2.9
Al_2O_3	--	4.1
NiO	--	0.9
CaO	--	1.5
Cl	--	0.05
Pb	--	0.05
F	--	0.06

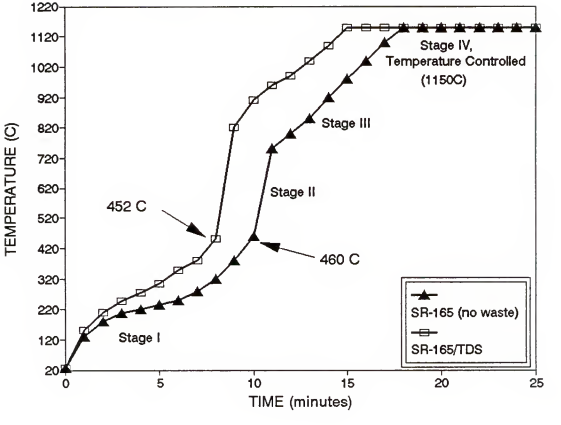


Figure 2-16. Results of the microwave heating rate experiments for the SR-165 and SR-165/TDS glass frits. Measured glass transition temperature for the SR-165 glass was ~476°C and ~462°C for the SR-154/TDS glass. Adapted from Schulz [Sch94b].

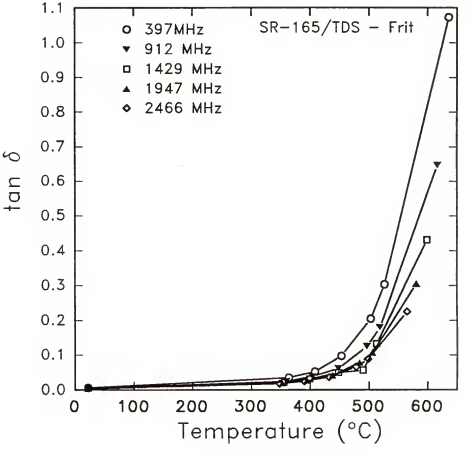


Figure 2-17. Tanδ versus temperature for the SR-165/TDS glass frit [Sch94b].

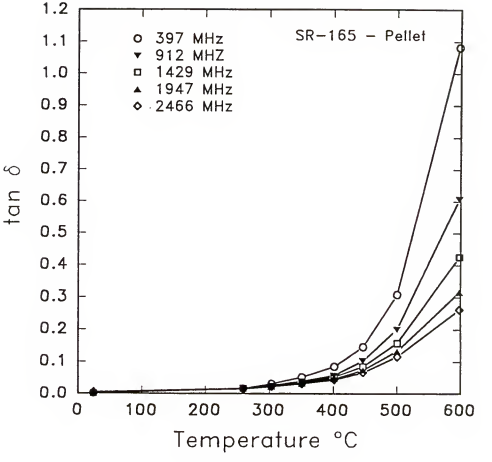


Figure 2-18. Tanδ versus temperature for the SR-165/TDS core-drilled glass sample [Sch94b].

varying lengths of time (0-60 minutes). Subsequent leach testing of the specimens using two standard leach testing methods indicated that the glasses processed for as little as 15 minutes performed as well as glasses processed for 24 hours in a conventional oven [Sch94b].

Sturken conducted experiments using a Wavemat (Model MCR-1300, Wavemat, Inc., Plymouth, MI) single mode microwave cavity and SiC crucibles to melt copper and aluminum as well as simulated nuclear waste glass frits [Stu91]. Sturken reported a more homogenized glass and theorized that this may be due to increased activity in the melt (bubbling due to the field intensity and thermal gradients) and that this action would eliminate the need for mechanical stirring that is required for some chemical reactions. The successful metal melting experiments were all carried out in an inert atmosphere to avoid oxidation.

White and researchers at Oak Ridge National Laboratory (ORNL) described the design and fabrication of a prototype continuous microwave melter for processing radioactive waste sludges. A schematic representation of the melter is shown in Figure 2-19. The melter used a 75 kW, 0.915GHz microwave applicator to process simulated ORNL dry sludge and frit. The composition of the surrogate waste feed consisted of 34.8wt% $CaCO_3$, 6.8wt% SiO_2, 4.2wt% MgO, 2.4wt% Fe_2O_3, and 1.8wt % $Al(OH)_3$. The frit was a mixture of sand or fly ash (33.5wt%) and $Na_2B_4O_7 \cdot 10H_2O$ (16.5wt%) [Whi96]. Simulated waste material was processed with the frit at a waste loading of approximately 44.7wt%. Significant volume reductions were achieved after processing at temperatures between

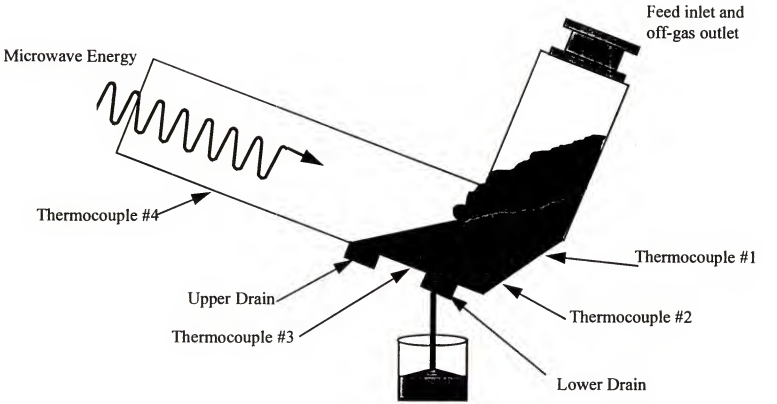


Figure 2-19. Schematic showing cut-away side view of the continuous microwave melter constructed at ORNL for processing radioactive waste sludges. Adapted from White, et al. [Whi96].

800-1000°C. Glass material was poured from the system after 10 and 20 minutes of processing. The density of the final glass product was approximately 2.7g/cm^3. Mention was made of plans for further characterization, but no additional data on the glass was provided. Researchers sited several of the advantages stated earlier in this section, primarily, the ease of start-up and cool-down, inexpensive equipment when compared to conventional systems, reduced floor space and flexibility of the equipment [Whi96].

The use of microwave energy for processing low-level radioactive waste has been investigated by several researchers [Law82, Shi89, Smi89, Mor93, Oda91]. Researchers at Ontario Hydro's Research Division investigated the use of microwave energy to dry or solidify radioactive sludge [Oda93]. A microwave applicator was positioned within a 45-gallon container of sludge and heated and subsequently dewatered the contents in-situ. Later experiments were conducted on much larger storage containers (4m^3) referred to as flasks. Prior to use on actual radioactive materials stored in the flasks, trials were carried out on wet sand analogues and were successful in removing enough water to warrant second phase tests on the radioactive waste. In both stages, the microwave applicator was positioned at the top of the flask at an angle that would permit the greatest heating uniformity. Existing inspection ports were utilized for exhaust of water vapor. The walls and top of the flask were insulated to improve heating efficiency. Total processing time was approximately 24 hours using a microwave power output of 28kW operating at 0.915GHz. Upon completion of the test, moisture content of the analogue was reduced from approximately 20% to less than 1%. For the radioactive waste, water content was sufficiently reduced to allow transport and storage as required by the Canadian Atomic Energy Control Board (sludge must contain no

free water) [Oda93, Oda94]. Researchers also reported advantages associated with microwave energy including; ease of use, a process that was simple to control and had minimal operator involvement.

Morita et al. used a 750W, 2.45GHz microwave (typical power and frequency found in home-use microwave ovens) to reduce the volume of simulated transuranic contaminated ash from Los Alamos National Laboratory [Mor93]. Temperatures in excess of 1400°C were achieved in as little as fifteen minutes following the addition of approximately 40wt% Fe_3O_4, a ferrimagnetic material. This was thought to be due to the high dielectric loss factor of Fe_3O_4. Addition of such materials has long been recognized as an aid or catalyst in heating materials that do not readily react with microwave energy. This may be expected as a material that exhibits magnetic losses at microwave frequencies can be treated with microwave energy as well [Met83]. As the expressions for energy dissipation in a magnetic material and a dielectric material are analogous (see equation 2-3), one may expect similar responses with exposure to alternating high frequency fields [Met83]:

$$\tan\delta_m = \frac{\mu''_{eff}}{\mu'}; \quad \tan\delta = \frac{\epsilon''_{eff}}{\epsilon'_r} \qquad 2\text{-}3$$

Where μ' is the permeability, μ''_{eff} is the effective magnetic loss factor due to relaxation and resonance processes under the influence of an alternating magnetic field, ϵ'_r is the relative dielectric constant and ϵ''_{eff} is the effective relative dielectric loss factor. Tanδ is an expression of energy dissipation, either magnetic or electric. This is discussed in more detail in Chapter 4.

Another material added to the mix in an attempt to improve heating was also attempted. Water was added to the ash mixture (mixed with 20wt% Na_2CO_3, 20wt% B_2O_3, 10wt% Fe_3O_4, 50wt% ash) and was also found to increase the heating rate in that 1400°C was reached in 9.7 minutes as opposed to 16.3 minutes without water. Other additives such as Li_2CO_3, B_2O_3, and Na_2CO_3 were added to improve the homogeneity of the melt [Mor93].

Non-radioactive wastes

Dauerman et al., identified and investigated the use of microwave energy for five separate waste streams [Dau92]. These included 1) soil contaminated with volatile and semi-volatile organics; 2) soil contaminated with non-volatile, insoluble organics; 3) soil contaminated with toxic heavy metals; and 4) spent granulated activated char (GAC), from wastewater treatment facilities. Their studies primarily focused on the physical chemical mechanisms involved in the development of a microwave remediation process for the specific types of waste mentioned above, as well as pilot plant and scale-up studies, if warranted.

For the first waste stream listed (soil contaminated with volatile organics), a scale-up economic feasibility study was conducted with a projected cost of 40$/ton. Conventional incineration techniques cost between $150-300/ton. Even though microwave processing technology appeared to be economically favorable at pilot plant levels, further field testing was considered necessary in order to eliminate any problems that may develop with larger scale-up operations.

For the second waste stream, soils contaminated with non-volatile, insoluble organics (i.e., dioxins), in-situ remediation was recommended by regulatory agencies

(Environmental Protection Agency (EPA)). According to EPA studies, the greatest risk in cleaning these sites arises from excavation and transportation of the contaminated soil. Microwave irradiation is readily adaptable for mobile applications, and is capable of generating the heat necessary to remove water from the soil causing the organics to become bound to the soil components (clay and humus). Further irradiation heats the soil to sufficient temperatures to cause fixation of the organics. Similar methods are necessary for toxic heavy metal contamination. However, greater temperatures are necessary in order to cause incorporation of the metals within the minerals present in the soil. If humus is present, absorption of microwave energy brings about the reduction of the heavy metals to less toxic states or to forms in which they can be more readily incorporated into clay minerals [Dau92].

Granulated activated char filters are used to remove organic contaminants from waste water. Over time, the GAC becomes water-logged and incapable of absorbing the organics. However, the GAC is now considered a hazardous waste and is generally shipped off-site for regeneration. Regeneration is possible on site using microwave technology, providing the correct atmosphere is maintained to prevent arcing and combustion of the filter [Dau92].

Researchers at Birmingham University in the United Kingdom have developed a process where coal/caustic slurries are treated with low-power microwave energy (600W) to reduce the amount of sulfur emissions. Sulfur in coal is frequently found as pyritic sulfur, FeS_2. Heating the coal with microwaves transforms the non-magnetic pyritic phase into the highly magnetic pyrhotite phase which facilitates removal via magnetic separation techniques. However, this process required a high-power microwave unit. An alternate technique was investigated using a caustic slurry. Upon irradiation, rapid leaching by the

sodium hydroxide solution forms a coating of iron oxides on the pyrite surfaces making them magnetic. A low intensity magnetic separation stage follows irradiation. Analysis of the resulting coal showed a sulfur reduction of 60 to 70% with little effect on the quality of the coal [Pro91].

Microwave energy has been tested for treating steel mill sludge [Goo96]. The sludge is made up of residues from cooling water, lubricating oils and metallic fines. Each year, approximately 1 million tons of sludge are generated by US steel mills. In laboratory scale tests, low temperature (53°C) microwave processing was used to separate oil/water emulsions. After 10 minutes of processing, separation to clear water was achieved. Conventional methods generally take up to 5 hours. Similar tests were conducted with magnetically concentrated oil-metallic wastes. After 10 minutes of processing, the microwave samples had achieved the same degree of separation of magnetic solids that required 24 hours using conventional techniques. Several patents have been granted for this technology [Wol86,Wol89, Hud88, Hud88a, Sam88, Sam 88a] and an economic analysis for the proposed scale-up system estimates cost savings of up to 50% for disposal costs alone. In addition, reclaimed oil could be reprocessed, and reclaimed metal could be recycled. As of the writing of the article (1996), plans were underway to conduct large scale (25-ton sample) testing of the process.

Researchers at Ontario Hydro working with an automotive supplier, reported using microwave energy to remove methylene chloride from polyurethane foam waste. The mixture of the chlorinated solvent (cleaning solvent) and foam are produced as a result of injection molding of automotive dashboard instrument panels. The waste mixture was

subsequently sealed in 45 gallon drums. In order to reclaim the solvent and to reduce the toxicity of the waste, microwave energy was applied in-situ to the waste material. A microwave applicator was fabricated to fit on the drum lid. Once activated, the microwave preferentially heated the solvent and allowed it to be recovered using distillation methods. Processing time for each drum was approximately 2 hours with a removal rate of 8kg solvent/kWh at a generator output of 2-3kW [Oda92].

Peterson [Pet97] reported using radio frequency and microwave energy (RFM) for separation of oil emulsions. The waste material to be processed had already been subjected to thermal recovery methods and was considered unbreakable sludge. The sludge consisted of 20% oil, 10% solids and 70% water (by volume). The general design of the apparatus is shown schematically in Figure 2-20 and uses standard microwave technology (power and frequency not specified due to pending patent applications) in combination with centrifuge separation techniques. The system has been in operation since 1996, with treatment runs lasting from 8-12 hours. Sludges were heated at temperatures between 135-150°F and at pressures of approximately 20 psig which was sufficient to keep the sludge flowing into the centrifuge. Conventional methods require temperatures ranging from 220-400°F with pressures of 250psig. Upon completion of microwave processing, three separate components were produced; pipeline quality oil, low solids water and a solid paste-like material. The reasons for the lower processing temperatures and pressures were attributed to the selective heating capabilities of microwave energy (coupling more efficiently with the polar molecules in the emulsion).

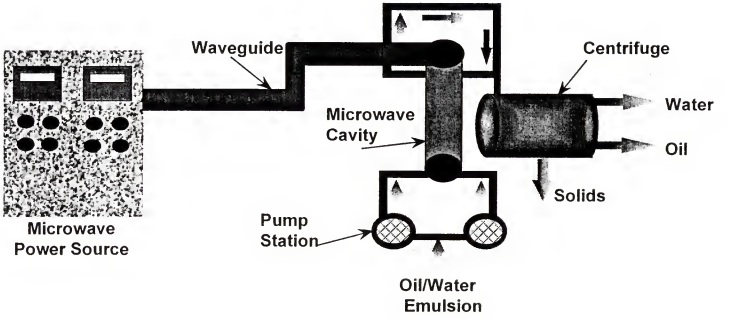


Figure 2-20. Simplified schematic of the Imperial Petroleum Recovery Corporation's radio and microwave frequency system for separation of oil emulsions. Adapted from Peterson [Pet97].

Bradshaw et al. [Bra97] demonstrated the use of microwave energy to regenerate carbon-in-pulp (CIP) granulated activated carbon filters. These filters are used in a gold reprocessing method where dissolved gold ore and aurocyanide are adsorbed onto the carbon. The gold is removed by elution and the carbon filters are acid washed and regenerated in a steam environment at temperatures between 650-850°C in an electrically heated rotary kiln. Bradshaw reported that by using microwave energy (0.915GHz) the filters regenerated at 600°C using microwave energy had a higher reactivity that those regenerated by other means, and that the operating costs for the microwave system would be less than those of the current rotary kiln system.

In a somewhat different area, Casasnovas et al. [Cas94] reported the use of microwave energy for sterilizing food packaging waste. In this process, the waste was shredded, compacted into cylinders, water was added and the cylinders were then subjected to various microwave power levels and over pressures, depending on the density and moisture content of the cylinder. It was demonstrated, on a laboratory scale, that microwave energy was successful in heating the cylinders and destroying certain bacteria (B. stearothermophilus), with adequate temperatures (250°C), pressures (15 psig) and processing times (60-101 seconds).

One area of microwave waste remediation that has been commercialized is in the area of sterilization of hospital wastes. According to the literature, the system has been approved for use in the both the US and Canada, and has been tested and operated in both countries since 1990 [San97, Str97, Ele97]. The system was originally designed in Germany and

introduced to the US in 1990 where since that time, approximately 30 facilities have installed the system.

The microwave unit (see Figure 2-21) does not use incinerator technology, as it has been proposed that disinfection is sufficient remediation for ~95% of the medical waste generated [Str97]. The bagged waste from medical facilities is hydraulically loaded into the unit where it is fed through the first of two shredding devices. A screw conveyor system moves the waste through the system where it is moistened with high-temperature steam and subjected to microwave energy through six sources in order to uniformly subject each granule. The waste material is held at temperatures in excess of 95 °C for 30 minutes. Upon completion of sterilization procedures, the waste is passed through the second shredder and into a collection container. The processed waste, that has been reduced in volume by approximately 85%, can then be sent to a landfill. By avoiding combustion, emissions should be greatly reduced when compared to those that can be expected from an incineration apparatus. Emissions generated are passed through a HEPA filter prior to release. Economic analyses of the system estimate operating costs of approximately $0.35/kilogram (1997 Canadian dollars, which converts to approximately $0.22 1998 US dollars/kg) based on a throughput of 1300 kilograms/day. This estimate includes maintenance and capital costs, as well as utilities (water and electric). Other advantages of the system include reduced space requirements and favorable public acceptance of the technology [Ele97, San97, Str97].

Gaseous Waste Forms

As this dissertation will focus to a large degree on the microwave/material interactions within the off-gas component of the microwave waste treatment system, the

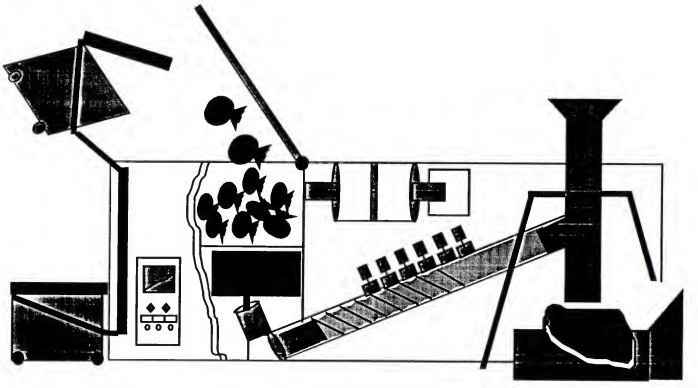


Figure 2-21. Simplified schematic of the Sanitec, Inc. biomedical waste disinfection system. Adapted from Sanitec, Inc. [San97].

following section will provide information on other applications of microwave energy used in the treatment of gaseous waste forms.

In 1991, researchers at Argonne National Laboratory reported using microwave energy to destroy gaseous wastes produced as a result of oil refinement and purification of natural gas. Microwave energy was used to decompose hydrogen sulfide gas and allowed the sulfur and hydrogen components to be isolated and recovered separately. The recovered sulfur can be sold for other applications and hydrogen can be used as a fuel. Remaining impurities are converted to carbon dioxide and water. Any unconverted hydrogen sulfide gas is mixed with incoming waste gases and sent back though the process [Mec91].

Two British researchers, Harper and Hansen investigated the use of microwave and radio-frequency radiation together with a fluidized bed of paramagnetic transition metal ions absorbed onto a ceramic matrix to destroy dioxins. The ceramic matrix was irradiated, which in turn heated the metal ions. The waste stream, which was in either a vapor or liquid form, passed through the headed bed where the pollutants were decomposed to less harmful substances [Che93].

Varma et al. [Var91] used microwave energy (2.45GHz, 6kW to detoxify trichloroethane (TCE). The TCE gas was passed through a bed of 80-mesh silicon carbide particles at temperatures ranging from 400-580°C and two flow rates (252 and 510cc/min). When compared to conventional heating methods, it was found that detoxification was more complete when the gas was subjected to microwave treatment. Breakdown products consisted of hydrochloric acid, carbon dioxide and carbon monoxide. Where conventional heating methods under similar test conditions were used for comparison, only partial

conversion of the TCE was achieved with the breakdown products consisting of dichloroethylene and hydrochloric acid.

Dauerman and Windgasse also reported using microwave energy to treat an organic gas stream by passing a mixture of TCE, helium, argon and water through a microwave heated granulated activated charcoal bed. Similar experiments were carried out using a silicon carbide bed, as well. Decomposition of the TCE was determined via gas chromatography and no TCE was detected after treatment. Presence of HCl acid was determined by precipitation chemistry [Dau92].

In a somewhat indirect method, Kong and Cha [Kon95] used microwave energy to increase the efficiency of a carbon absorbent bed used to remove NO_x emissions from the flue gases. In this study, flue gases were passed through a variety of different carbon beds, which absorbed the NO_x emissions. When the bed was saturated, microwave energy was used to regenerate the material. Upon exposure to microwave energy, the NO_x reacted with the carbon, forming nitrogen gas and carbon dioxide. As carbon is consumed during this process, the bed becomes more porous and internal surface area is increased allowing for even greater absorption of NO_x upon reuse. The researchers state that as much as 90% of the NO_x that was absorbed on certain char beds could be recovered and that the method was applicable to both small-scale (diesel engines) and large-scale commercial operations (industrial heaters).

Similarly, Bathen and Schmidt-Traub [Bat97] also demonstrated the use of microwave energy for regeneration of activated carbon and zeolite adsorbents. When compared to conventional regenerating methods, the microwave process required one-third

the amount of desorbing gas, shorter processing times and lower operating temperatures.

In an innovative approach to remediate certain types of air pollution, Nusinovich et al. [Nus95] proposed the use of microwave generated plasmas to remove halocarbons (i.e., CCl_4, CCl_3F) from the atmosphere. In this technique, microwave generators would be located near the source of the contamination and intermittently pulse microwave energy to generate an atmospheric plasma which in turn, would create free electrons. Once the free electrons cool due to collisions with air molecules, the electrons could then attach themselves to molecules in the halocarbons, destroying the halocarbon and effectively cleansing the air.

In the above sections a description of the laws and regulatory requirements concerning solid and gaseous wastes was provided. Summaries of conventional air pollution devices was provided along with EPA approved gas sampling methods. In addition, a literature survey of some of the research being done in the area of microwave waste remediation for solids, liquids and gases was furnished. In the following chapter, the materials, equipment and procedures used for the waste remediation studies carried out for this work are provided.

CHAPTER 3
MATERIALS AND EXPERIMENTAL PROCEDURES

Introduction

In the first section of this chapter, the materials used to fabricate the primary constituents of a printed wire board are discussed. The second section provides information on the experimental procedures used throughout the study. In the third section, a discussion of equipment developed and fabricated for the various studies involving recycling of printed wire/circuit boards and destruction/decomposition of emissions is provided. Characterization methods are discussed in the final section.

Printed Circuit (Wire) Boards

Each year, many thousands of tons of circuit board scrap material become obsolete [Dun80, Dun83, Lip93, Wic97]. A large portion of this material is disposed of in landfills. This action causes a tangible loss of valuable recoverable resources. The studies described in this text constitute a concerted effort to offer an alternative disposal/recovery program using microwave energy for reducing the volume of the waste form, recovering the metal components, encapsulating any hazardous constituents while simultaneously treating the emissions that arise from the treatment process.

The materials used in this study consisted of a wide variety of printed circuit or wire boards (CB/WB). Most of the boards were salvaged from various commercial- or defense-

related activities and were components in products such as, computers, printers, monitors, televisions, video cassette recorders, telephones, police scanners, radios, or weapon's systems as shown in Figure 3-1. The boards acquired from the Pantex Corp. had specialized defense-oriented applications. Circuit boards are generally classified and graded according to the resin/reinforcing material as shown in Table 3-1 by the National Electrical Manufacturers Association (NEMA). Some properties of the various grades of circuit boards are also provided in Table 3-1 [Har94]. Table 3-2 provides some characteristics and applications for the many types of polymeric materials found in the printed wire board package. Physical, thermal and electrical properties for common polymers used in the electronic industry are shown in Table 3-3.

Matrix Materials

The primary matrix materials used in the manufacture of most composite printed wire or circuit boards are epoxy, phenolic (cross-linked, thermoset plastics) or polyester resins, or polyimides. Approximately 90% of the thermosets used for wire boards in the US are epoxy-based. Epoxy resins are selected because they possess the properties necessary for use in a laminated electronic device, are relatively easy to work with, and are generally low in cost (see Table 3-4). The most important properties include high adhesive and mechanical strength, good electrical insulation properties, low shrinkage, chemical resistance, thermal stability, curability, and the ease with which modifications can be made to optimize performance. The most commonly used epoxy resin is diglycidyl ether of 4, 4'-bis(hydroxphenyl) methane [Maz90,Coo88]. The polyimide resin used most frequently for lamination purposes is based on bis-maleimides (BMI) and has higher end-use

Figure 3-1. Photograph showing circuitry available for recovery operations in some common household equipment.

Table 3-1. NEMA Grades, Descriptions and Properties of Printed Wire Boards [Har94].

GRADES 11-1-1989	XXXP	XXXPC	FR-1	FR-2	FR-3	FR-4	FR-5	FR-6	CEM-1	CEM-3	G-10	G-11
Fabric	paper	paper	paper	paper	paper	E-glass fabric	E-glass fabric	E-glass matte	E-glass cloth surface, cellulose paper core	E-glass cloth surface, nonwoven glass core	E-glass fabric base	E-glass fabric base
Resin	phenolic	phenolic	phenolic	phenolic	epoxy flame resistant	epoxy flame resistant	epoxy flame resistant	polyester flame resistant	epoxy flame resistant	epoxy flame resistant	epoxy general purpose	epoxy temp. resistant
Dielectric Constant @1 MHz	4.80	4.80	6.00	4.80	4.80	5.40	5.40	4.30	5.20	5.40	5.40	5.40
Loss Tangent @ 1 MHz	0.040	0.040	0.060	0.040	0.040	0.035	0.035	0.030	0.035	0.035	0.035	0.035
Flexural Strength 10^3 lb/in^2 crosswise	10.5	10.5	10.0	10.5	16.0	50.0	50.0	--	40.0	40.0	50.0	50.0

Table 3-2. Characteristics and Applications of Selected Polymers Used in Electronic Components [Har94].

Material	Characteristics	Applications
Acrylics	clarity, good surface hardness, chemical and environmental resistance, mechanical stability	electronic display filters, coatings
Epoxides	chemical and environmental resistance, mechanical stability	encapsulants, coatings, circuit boards
Fluoroplastics	heat and chemical resistance, low dielectric losses, low friction coefficient	wire insulation, electrical components
Ketone resins	heat and chemical resistance, high strength, resistance to burning, thermal and oxidative stability, good electrical properties, low smoke	wire insulation, cable connectors
Liquid Crystal Polymers	high temperature and chemical resistance, high mechanical strength, low CTE	chip carriers, sockets, connectors, relay cases
Nylon	mechanical strength, tough, abrasion and wear resistance, low friction coefficient	connectors, wire jackets, wire ties, coil bobbins
Polyamide-imide	high temperature resistance, good mechanical properties, creep and chemical resistance, radiation resistance	connectors, circuit boards, radomes, films, wire coatings
Polyacrylate	UV stability, heat resistance, stable electrical properties, flame retardant	connectors, coil bobbins, switches, fuse covers, relay housings
Polycarbonate	clarity, toughness, heat resistance, flame retardant	connectors, terminal boards, bobbins
Polyesters	good electrical properties, chemical resistance, high temperature resistance	connectors, sockets, chip carriers, switches, coil bobbins, relays
Polyetherimide	high temperature strength, dimensional stability, chemical resistance, low smoke generation	connectors, low loss radomes, circuit boards, chip carriers, sockets, bobbins, switches
Polyimides	superior high temperature properties, radiation resistance, flame resistance, good electrical properties	insulation for motors, flat cable, integrated circuit applications
Styrenes	low dielectric losses, wide range of properties depending on type of styrene	housings, capacitor dielectrics
Polysulfones	high temperature resistance, good electrical properties, radiation resistance	circuit boards, connectors, TV components
Vinyls	range of properties depending on type of vinyl	wire insulation, tubing and sleeving

Table 3-3. Physical, Thermal and Electrical Properties of Selected Polymers Used in Electronic Components [Har94].

Material	Dielectric Constant at 60 Hz	Loss Tangent at 60 Hz	CTE (10^{-5}in/in/°C)	Flammability (in/min)	Heat Resistance (°C)	Tensile Modulus (10^2lb/in^2)
Acrylics	3.3-3.9	0.04-0.05	-9	9 - 1.2	54.4 - 90.6	350-450
Nylon 6	10^{14} - 10^{15}	0.4-0.6	1.1 - 8.0	self-extinguishing	65.6 - 79.4	9.5-12.4
Polycarbonate	6.1 x 10^{15}	0.0001-0.0005	6.7 - 7.0	self-extinguishing	121.1	345
Polyetherimide	6.7 - 10^{17}	0.0013	4.7 - 5.6	self-extinguishing	165.6 - 176.7	430
Polyethylene (medium density)	10^{15}-10^{18}	0.0001-0.0005	10 - 20	slow burning	65.6 - 82.2	50-80
Polyimide	10^{16} - 10^{17}	0.002-0.003	4.5 - 5.6	--	260 - 315.6	300
Polypropylene	10^{15}- 10^{17}	0.0007-0.005	3.8 - 9.0	slow to non-burning	--	--
Polystyrene	10^{17} - 10^{21}	0.0001-0.0005	5 - 8	0.5 - 2.5	65.6 - 87.8	400-500
Polysulfone	5 x 10^{16}	0.0056-0.008	5.6	self-extinguishing	149	360
Polytetrafluoroethylene	> 10^{18}	<0.0001	2 - 12	nonflammable	260	50-80
Polyvinyl chloride (flexible)	10^{11} - 10^{15}	0.08-0.15	7 - 25	self-extinguishing	65.6 - 79.4	--
Polyvinyl chloride (rigid)	10^{12} - 10^{16}	0.01-0.02	5 - 10	self-extinguishing	71 - 73.9	200-600

Table 3-4. Properties of Selected Resin Materials [Har94].

Material	Dielectric Constant at 60 Hz/10^6Hz	Loss Tangent at 60 Hz/10^6Hz	CTE (10^{-5}/°F)	Thermal Conductivity BTU•in(h•in•ft^2•°F)	Tensile Strength lb/in^2
Glass-Filled Epoxy	5.0/4.6	0.01/0.01	1.7	6	30000
Mineral-Filled Epoxy	4.0/5.0	0.01/0.01	2.2	--	15000
Glass-Filled Phenolic	50.0/6.0	0.3/0.8	--	0.34	7000
Mineral-Filled Phenolic	6.0/10.0	0.07/0.10	0.88	0.2	11000
Polyimide	3.5/3.4	0.0025/0.01	2.8	6.8	17000
Bismaleimides	--/3.5	--/0.007	40ppm/°C	--	12000
Polyester (GPO-3)	4.5/--	0.05/--	2	4	9000

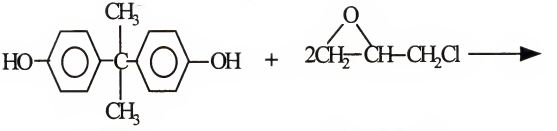
temperatures than the epoxy resins mentioned above, but is more expensive [Sch89, Coo88]. Some relevant properties of selected resin materials were listed in Table 3-4. An in-depth discussion of the compounds used to create the resins used in wire/circuit boards follows.

As mentioned earlier, the most commonly utilized epoxy is the diglycidyl ether of bisphenol A (DGEBA). The chemical formulae for the starting compounds for DGEBA, as well as the formula for the end product are shown in Figure 3-2 [Maz90].

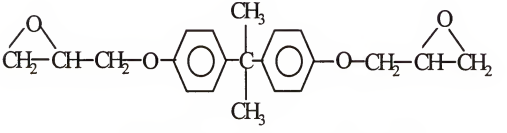
Bisphenol A is formed from the reaction between acetone and phenol. The epichlorohydrin is derived from propane. The molecular weight of the DGEBA is 340 amu, however, this is often altered by adjusting the amount of epichlorohydrin, or changing the pH. Adjustments are made to the base formula to change viscosity or melting temperature.

The second stage in the formulation of DGEBA resins is the reaction between the resin and an additive often referred to as a hardener or curing agent. When the DGEBA resin and curing agent are mixed, a highly crosslinked network is formed. The primary reasons for crosslinking or "curing" the resin are to improve adhesive properties, chemical, thermal and mechanical stability, and to increase storage life of the product. Many different types of curing agents can be used depending on the desired end properties and consist of numerous classes of chemical compounds. However, metaphenylenediamine (MDPA), 4,4'-methylenedianiline (MDA) or diaminodiphenyl-sulphone (DADS) are the most commonly used curing agents and have the chemical formulae shown in Figure 3-3.

In order to obtain the ultimate set of desired properties, filler or extender materials are often added to the resin-hardener system. Fillers are generally non-reactive and include materials such as: silica, talc, alumina, pigments, mold release agents and various other



Bisphenol A Epichlorohydrin



Diglycidylether of bisphenol A (DGEBA)

Figure 3-2. The chemical formulae for the starting compounds for diglycidyl ether of bisphenol A (DGEBA), as well as the formula for the end product [Maz90].

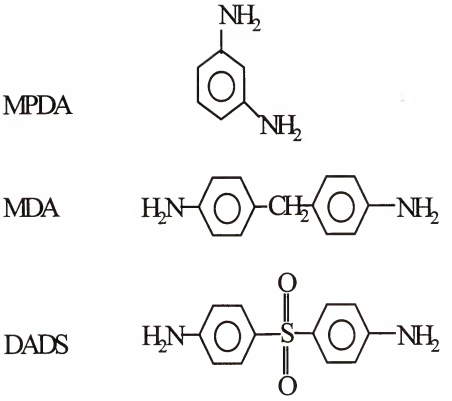


Figure 3-3. The three most common epoxy resin curing agents [Maz90, Har94, Har94a].

minerals. They are often added to reduce cost, decrease the coefficient of thermal expansion, increase thermal conductivity, increase hardness, improve strength, alter the dielectric strength, reduce creep, and improve flame retardance. Extensive manipulation of these three groups of materials is often necessary in order to attain a wire board matrix that meets the majority of the preferred end properties for the matrix material.

Reinforcing Materials

The two principal materials used as reinforcements for printed wire boards are paper and E-glass. In some special applications, other reinforcements are selected and can include quartz, aramid fibers (Kevlar), ceramic spheres, S-glass, or a combination of reinforcing materials designed to optimize end-use properties. The compositions of E-glass and S-glass fibers are shown in Table 3-5 and relevant physical properties of some the main reinforcing materials are shown in Table 3-6.

Paper reinforcements are used with flame retardant resins, primarily in boards where dimension stability is not of critical importance. Use is limited to single or double-sided boards where holes are punched through the laminate. End-use applications include items such as, toys, calculators and radios [Har94a].

The fiber that is used for most reinforcement applications is E-glass. The fiber reinforcement can take the form of randomly oriented glass fiber mats or woven fabrics. The E-glass reinforcements can be used in single, double and multi-layer WBs and are found in a wide variety of applications such as, aerospace, computer, communication, and industrial components.

Table 3-5. Compositions of E-Glass and S-Glass Fibers [ASM88].

Component	E-Glass (wt%)	S-Glass (wt%)
SiO_2	54.3	64.2
CaO	17.2	0.01
Al_2O_3	15.2	24.8
B_2O_3	8.0	0.01
MgO	4.7	10.27
NaO	0.60	0.27
FeO	--	0.21
BaO	--	0.2

Table 3-6. Relevant Properties of Some Reinforcing Materials Used In Printed Wire Boards [Har94a].

Property	E-Glass	S-Glass	Quartz	Kevlar
Specific Gravity (g/cm^3)	2.54	2.49	2.20	1.40
Dielectric Constant (@ 1 MHZ)	5.8	4.52	3.5	4.0
Tensile Strength (kg/mm)	350	475	200	400
Softening point (°C)	840	975	1420	300
Thermal Conductivity (W/(m•°C)	0.89	0.9	1.1	0.5
Coefficient of Thermal Expansion (ppm/°C)	5.0	2.8	0.54	5.0 (along fiber axis)

Quartz, Kevlar and S-glass fabrics are relatively new reinforcing materials and are generally used in WBs that require a lower dielectric constant than that of E-glass. Because these fibers are more expensive than E-glass, the end-use products are more specialized and WBs with these types of reinforcement are found primarily in military and aerospace applications.

Metal Components

Metals are used in a variety of capacities on printed wire boards. Copper is used almost exclusively to create the interconnect circuitry. To create the interconnect layer, electrodeposition of the copper is the method of choice. Electrodeposited copper layers are classified according to their specific uses and with respect to their weight per unit area (oz/ft^2). An alternative method for creating the interconnect layer is to use wrought films. Wrought films are often used in specialized cases where high ductility is essential, as in flexible circuitry.

In addition to copper, several other materials are also used as interconnect materials, primarily for special use applications. Aluminum is used in a limited capacity as an interconnect layer in applications where weight restrictions are critical. Copper-clad materials such as copper-clad Invar (CIC) and copper-clad molybdenum (CMC) are used in applications requiring controlled coefficients of thermal expansion (CTE). The thickness ratio of Invar or molybdenum controls the CTE of the clad metal.

Surface Mount Components

In the above sections, a discussion of the principal materials used to create printed wire boards was provided. However, most of the materials used in this study contained not

only the printed wire board itself, but the ancillary components contained on the board as well. This includes a wide variety of components such as chips (leaded or leadless), chips mounted on substrates or chip carriers, capacitors (both single and multi layer), semiconductors, heat sinks, magnetic components, resistors, insulators, wires, connectors, and many others. These components consist of wide range of polymeric, ceramic and metallic materials and are too broad a category for an elaborate discussion in this text. However, a schematic outlining the steps and materials used in the formation of a typical multilayer capacitor are shown in Figure 3-4. A summary of some of the primary materials found in all types of surface mount components is shown in Table 3-7.

Circuit Board Manufacturing and Assembly Processes

The manufacturing process for single or double-sided reinforced printed circuit boards involves several basic steps as shown in the flowchart in Figure 3-5. Pre-production phases begin with the design and layout of the circuitry pattern and are created using computer-aided design and manufacturing (CAD/CAM) processes. The circuitry pattern or artwork is transferred to the PWB using either photo or screen printing. Most manufacturers favor photo printing techniques because it is not possible to create line widths smaller than 0.012 inches consistently with screen printing techniques. The pattern is brought in contact with a resist-coated PWB layer and the resist is exposed to a carefully controlled degree of ultraviolet light. After the exposure process, the unexposed photoresist is removed in a cleaning process referred to as the development stage. Etching of the copper foil to create the actual circuit pattern follows. Once the circuit pattern has been etched in the copper foil,

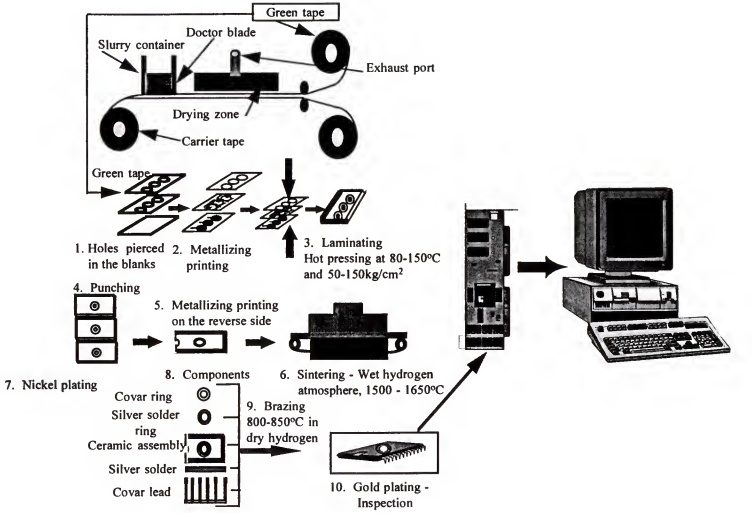


Figure 3-4. Process for manufacturing multi-layered ceramic packages used to house integrated circuits used in a variety of electronic devices such as TVs, VCRs, stereos, and computers.

Table 3-7. Main Materials Used in Surface Mount Devices [Har94].

APPLICATION	Insulators	Substrates	Resistors	Semiconductors	Coatings/Sealants	Capacitors
MATERIAL	αSiO_2, AlN, BeO, BN, Si_3N_4 Corderite, Diamond, Fosterite, Mullite, Porcelain Spinel ($MgO{\bullet}Al_2O_3$) Steatite ($MgO{\bullet}SiO_2$) Glasses, Glass-Ceramics	AlN, BeO, SiC, PSZ, Glasses	Cu-Ni, Cu-Mn, Cu-Mn-Ni, Ni-Cr-Al (Cu,Fe or Mn) Ni-Cr-Al-Mn Ni-Mn-Al-Si, Ni-Fe, Ni-Cr-Fe, Fe-Cr-Al Al,Cu,Au,Fe,Mo, Ni, Pt, As, Ta, W	GaAs, αSiC, BN,BP, Diamond,Silicon, GaSb, GaP, InSb, InAs, IP, CdS, CdSe, CdTe, ZnS, PbS, PBTe Dopants: Au, Ag, Cu, Mg, Ca, Zn, Cd, Se, Co, Ni, Sb, B, Sn, Mn	Glasses, diamond,	$BaTiO_3 + CaZrO_3$, $TiO_2 + CaTiO_3$, Mg_2TiO_4 or $MgTiO_3$

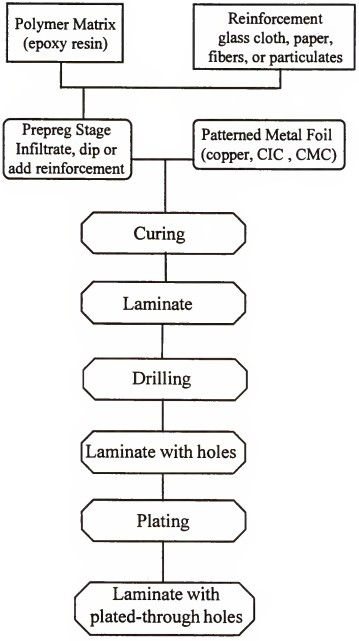


Figure 3-5. Flowchart showing basic steps in fabricating a reinforced circuit board. Adapted from Chen, et al. [Che95].

the photoresist image is stripped from the board using a solvent and the various internal layers are subjected to a lamination process [Har94].

The process begins by impregnating glass cloth with the selected resin, evaporating the solvents and partially curing the resin as shown in Figure 3-6. This yields a stable composite material that is referred to as the "prepreg." The prepreg is cut to the desired size and stored in sealed bags in a controlled and temperature and humidity environment until needed. The next step in the process is to produce the core, which involves laminating several layers of the prepreg with a suitable metallic (copper, CIC,CMC or aluminum) foil at elevated temperatures and pressures (170-180°C, 250-1000 psi) which fuses and cures the resin [Sch89, Maz90,Coo88]. The final steps in the preparation of the circuit board involve cutting the laminate to the desired size and mounting the various components on the board, depending on its specified end use.

Sample Preparation

All circuit board samples used in this study were prepared using procedures established during previous studies and are outlined in Figure 3-7. Because one of the original goals of the waste remediation work on scrap electronic defense circuitry was to "destroy beyond all recognition" it was discovered early on that it was more efficient to mechanically breakdown the circuit board into smaller pieces prior to processing, thus assuring the anonymity of all components both before and after processing. This was accomplished by first sectioning the board into pieces approximately 1 in^2 using a ban saw. The pieces were then passed through a Braun V67 Chipmunk Pulverizer to crush the remaining intact chips, resistors and capacitors (see Figures 3-8, 3-9). This process was

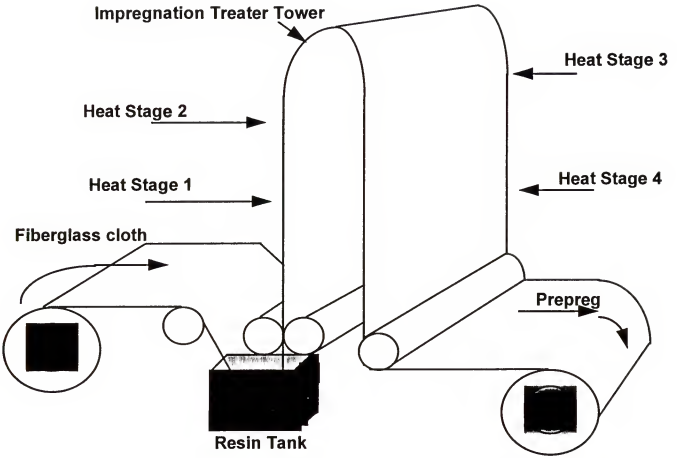


Figure 3-6. Basic fabrication process for epoxy resin prepreg. The fiberglass cloth is immersed in resin and is then heated to partially cure the resin and wound a spindle for storage.

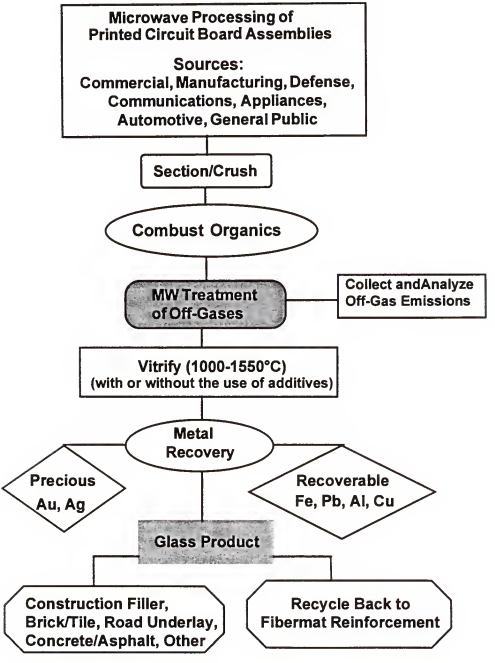


Figure 3-7. Flowchart showing processing procedures for the electronic circuitry waste.

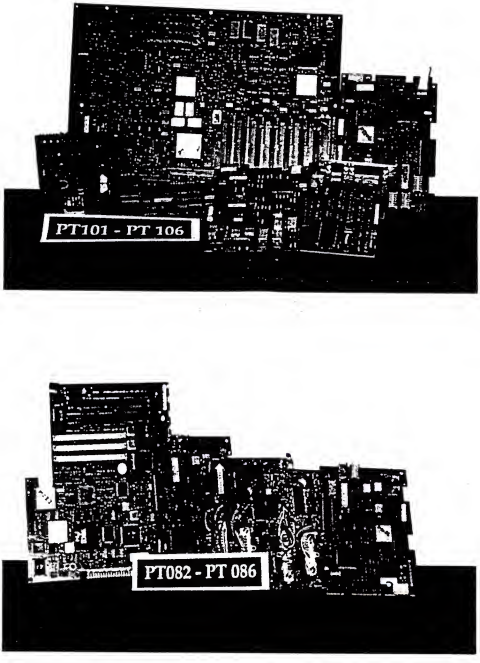


Figure 3-8. Digital photographs depicting representative defense circuit board waste from Pantex Corp.

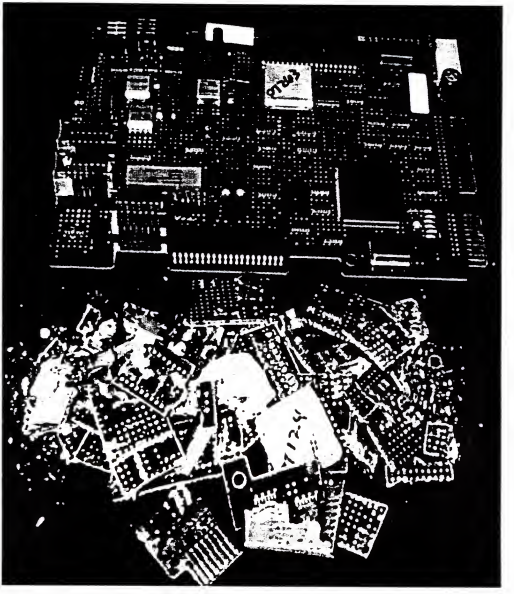


Figure 3-9. Digital photograph showing circuit board used in parametric study. Intact board in the top section and the same board after sectioning and crushing (bottom).

efficient in destroying the recognizability of the components and also made it more convenient to process the samples in available crucibles.

Once the components were sectioned and crushed, samples were weighed out, placed in fused silica crucibles and the organic constituents were removed via microwave irradiation (see Figure 3-10).

Equipment Development

The microwave equipment used for the treatment of the organics and the resulting off-gases during remediation of electronic components consisted of modified home or commercial microwave ovens. An industrial microwave (Raytheon Radarline Model (Model QMP-2101B-6), was used during the vitrification/metal recovery stages. Fused silica or alumina crucibles were used to contain the sample material and a variety of different refractory materials were used to protect the cavity and electronic components of the microwave units during sample processing. The equipment used during the course of this investigation underwent a series of modifications and improvements. In order to provide the reader with a clear picture of these modifications, a description of the various stages of equipment evolution and materials required are provided below.

Initial Air Pollution Abatement System

Preliminary combustion experiments were carried out using a Goldstar 800W, 2.45GHz microwave (model # ER-760M). All combustion experimentation was carried out in a fume hood. However, it soon became apparent some form of air pollution control would have to implemented to reduce the amount of emissions that were being released into the environment as a result of the treatment regime. To accomplish this, several modifications

Figure 3-10. Photographs of the initial stages of removal of organic compounds from the printed wire boards.

were made to the microwave oven. As shown in Figure 3-11, a tube was inserted through the external housing of the microwave and connected to a flange positioned within the microwave cavity. The opposite end of the tube was connected to a cold finger condenser and a second tube was run from the condenser to a vacuum pump. The condenser was inserted into a dewer filled with liquid nitrogen. During processing of the circuit board material, the vacuum pump was activated and gases were removed from the cavity and were condensed into liquid form in the cold finger. This apparatus was fairly effective in removing and trapping the bulk of the gases from the cavity. However, because the cavity was not air tight, some emissions escaped the cavity through the small crevices between the microwave cavity and the door and other manufactured openings in the cavity (i.e., exhaust opening, light fixture) As experimentation continued and successful results were obtained with regards to volume reduction, the scope of the study expanded. Soon it became apparent that the cold finger condenser/vacuum apparatus would not be adequate for larger samples and was not very amenable to anticipated scale-up plans. Therefore, another means of remediating the circuit board emissions was necessary.

Horizontal Microwave Waste Remediation System

Since microwave energy was used in the treatment of the circuit boards, it seemed only natural to use microwave energy to treat the emissions as well. A review of the literature in this area revealed that other researchers had some success using microwave energy in treating specific types of emissions (single gases) and therefore, the concept of using microwave energy to treat a mixed gaseous waste form was not unfounded. It was also known that in most cases, temperatures of 1000°C were successful in destroying or

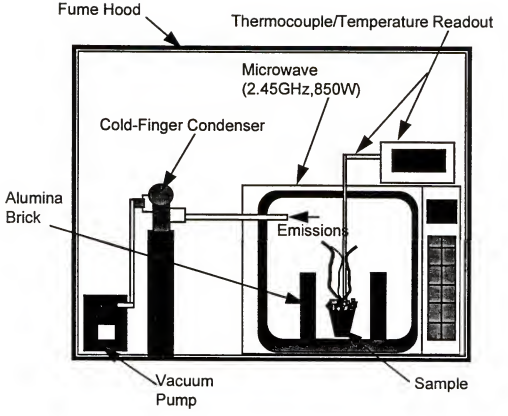


Figure 3-10. Initial air pollution abatement system utilizing a vacuum pump and liquid nitrogen condenser.

decomposing most known organic materials [Myc95]. Attaining such temperatures using microwave energy was easily accomplished. Therefore, a material that would permit the easy flow-through of the gases and had suitable dielectric properties was necessary. Silicon carbide in particle form was readily available and had the desired dielectric properties (tan δ =1.2-1.3 @ room temperature, 1-3 GHz) [Bat95]. Within the microwave off-gas chamber, the emissions would be simultaneously exposed to microwave energy and high temperatures. Thus, in theory, destruction/ decomposition of the gaseous waste prior to release to the atmosphere should occur, given sufficient temperature and residence time within the chamber.

In building the microwave waste treatment system, several other factors were also considered. These included the ability to withstand high temperatures, resistance to chemical corrosion, flexibility in process control and cost. Because of the heat and gases generated during processing of the circuit boards and the high temperatures that would be maintained in the off-gas chamber, it was felt that home model microwave ovens that generally have enameled walls and plastic components within the cavity would not be suitable for the rigorous environment created during processing of the waste electronic circuitry. However, commercial heavy-duty microwave units with stainless steel cavities were an appropriate alternative and would fit within the economic constraints of the project. While these units contained some plastic components within the cavity, appropriate use of refractories and re-design of the mode-stirring apparatus made the units acceptable for the project. Another feature that was considered necessary was power level or duty cycle control (duty cycle refers to the percentage of time within a given time interval that the magnetron is active or

operating). Both units eventually selected and purchased for the project allowed the operator to select and alter operating parameters such as processing time and duty cycle.

Once the microwave ovens were received, modifications were initiated. It was necessary to provide inlet access for thermocouples and compressed air. Also, openings had to be created to allow the emissions to pass from the combustion chamber to the off-gas chamber and from the off-gas chamber to the fume hood. In order to more efficiently handle the volume of emissions, was decided that exhaust openings would need to exceed the recommended safe aperture size for a microwave operating at 2.45GHz ($\sim \lambda/4 = 1.2$ inches) [Met83]. Therefore, some type of microwave choke or trap would have to be incorporated in the design to prevent microwave leakage. To accomplish this, a circle of the desired diameter (~2 in.) was scribed on the inner microwave wall and approximately 50-60 holes (1/16th inch in diameter) were drilled within the inscribed area. This modification allowed the emissions to be released from the combustion chamber while preventing microwave leakage. Similar modifications were made to the inlet and exhaust openings of the off-gas chamber. Any rough edges were removed using a metal file and SiC grinding paper to prevent arcing within the cavity.

The placement of inlet and exhaust openings as well as the geometry of the apparatus was dictated by the placement of the waveguide and microwave antenna. For the units used in the study, the waveguide ran along the top of the cavity and the mode stirrer was affixed to the top of the cavity and acted as an antenna directing the microwaves into the cavity. One of the blades of the stirrer was metallic and served to perturb the various microwave modes within the cavity. Perturbation of the modes provided more uniformity in the overall electric

field and more uniform heating of the sample [Met83]. Because of the placement of the waveguide at the top of the cavity, it was necessary to adopt a horizontal geometry for the waste treatment system as shown in Figure3-11. The compressed air inlet on the combustion chamber was through the right side of the oven and passed through the cavity electronic control/magnetron compartment. The emission outlet was situated directly across from the air inlet, on the opposite wall of the cavity. During processing, the sample was placed in the air flow pathway allowing the emissions to flow out of the combustion cavity, through the off-gas interconnect and into the microwave off-gas chamber for treatment. This system was successfully used to process many different types of circuit boards, as well as several other waste materials. However, it was believed that the system could be made to function even more efficiently with further modifications and changes to the overall design of the system.

Vertical Microwave Waste Processing System

The latest iteration of the microwave waste treatment system is shown schematically in Figure 3-12. This system was constructed using Goldstar Multi-Wave (MA-1164M, 850W (off-gas unit) and MA1280M, 900W (combustion chamber)) microwave ovens. According to the manufacturer, these microwave models have a rather unique method for launching microwaves into the cavity by using a split waveguide which directs the microwaves to two different areas of the cavity increasing the uniformity of the field within the cavity without the use of a mode stirrer. The design of this particular microwave allowed the use of a vertical geometry for waste treatment system. The microwaves also had the option for power level control and were relatively inexpensive to purchase should the need arise to replace them.

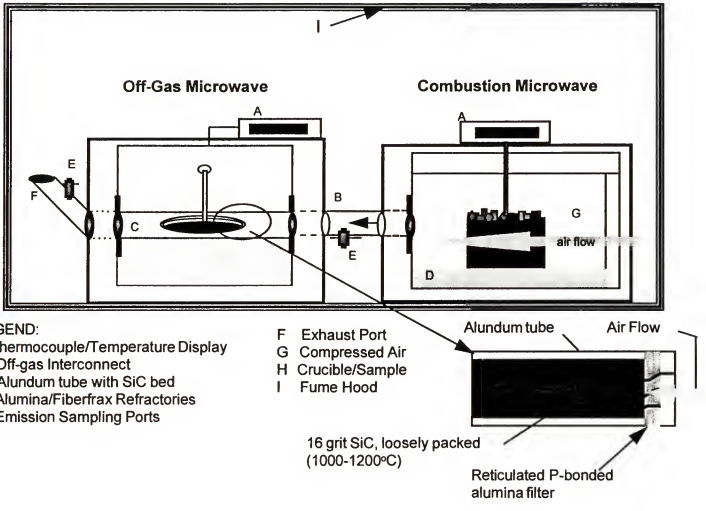


Figure 3-11. Schematic representation of the horizontal microwave waste treatment system.

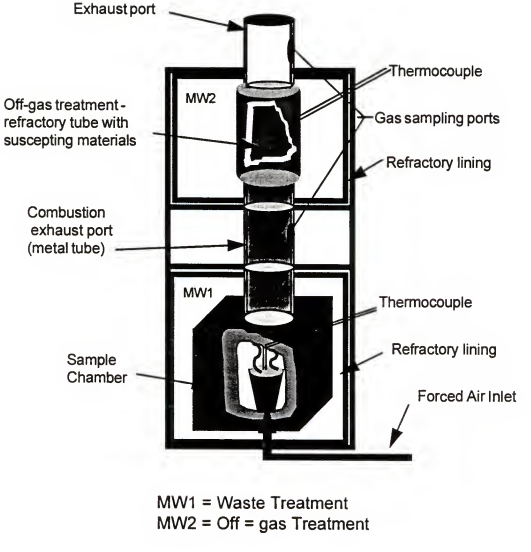


Figure 3-12. Schematic representation of the vertical microwave waste treatment system.

Single Gas - Toluene Experiments

To better understand the effects of flow rate and temperature within the microwave off-gas system, it was decided that introducing a controlled amount of a single material would be beneficial. This initiative would hopefully provide a known starting point for all experiments with reductions in concentration after microwave treatment due solely to changes in processing parameters, rather than variations in initial feed material or fluctuations in the volume of the waste gas species. However, the data collected could not be considered quantitative as a mass balance could not be calculated without knowing the amounts of carbon dioxide, water vapor and other decomposition products generated. Toluene was selected for use in the study because it was generally found in the waste emissions generated during processing of electronic circuitry, was readily available and had fewer health risks associated with its use when compared to some of the other gases considered (benzene).

For each experiment, the air flow rate was adjusted to either 10, 30 or 50 scfm. Temperature of the off gas unit was pre-set to 400, 700, or 1000°C and the Tenax air traps were positioned in the sampling ports. Liquid toluene was then introduced to the compressed air line through a septum using a gas-tight glass syringe. The septum was positioned approximately 5 feet from the lower microwave chamber air inlet opening in order to allow adequate mixing and vaporization of the toluene before it reached the pre-microwave treatment gas sampling port and the off-gas chamber (either microwave or conventional heating). Toluene was injected incrementally (100μl/minute) until the total amount to be injected was delivered to the air stream (1000μl).

Pantex Defense Electronic Circuitry Experiments

A parametric study was planned for the materials received from the Pantex defense waste processing facility in Texas. The circuitry was shipped to the WSRC laboratory in a 55 gallon drum. The contents of the drum were photographed and inventoried. An example of the inventory sheet designed to keep track of the samples as they progressed through the processing scheme is shown in Figure 3-13. Once inventory and photography was completed, the circuit boards were boxed and shipped to UF for sectioning and crushing. The boards were re-weighed after crushing, and the weights recorded on the inventory sheets. Completed inventory sheets were returned with the samples. After examining the individual boards and the tabulating the supply from the inventory sheets, a specific board was selected for the parametric study (board number 6370743-620-05). This board type was selected because there was sufficient quantity to carry out the study.

To begin the study, all the selected crushed boards were first combined together. Then, in order help ensure a somewhat uniform feed, the circuit board laminated material was separated from the crushed chips and other surface mount material that detached from the boards during the crushing operation. For each experiment, approximately 25 grams of laminate material and 9.5 grams of surface mount material was used. Processing time was 15 minutes. The sample material was placed in a fused silica crucible. The crucible was situated within the Rath refractory cylinder and a K-type Inconel-shielded thermocouple was positioned in the sample. A Kaowool board cover with a circular opening was placed on top of the setup and the entire assembly was positioned beneath the opening of the off-gas interconnect. An air flow rate was selected and the Tenax air tubes were positioned inside

WSRC INVENTORY CONTROL SHEET

SAMPLE ID	CB NUMBER	WEIGHT (g) initial	Post crush	STATUS Sent UF	Ret WSRC
PT001	03233-00101	922.60			
PT002	202051/202054	563.45			
PT003	30529304V	269.46			
PT004	20383	211.23			
PT005	6370917 110 02	185.17			
PT006	6370743 11005	194.55			
PT007	163854	162.82			
PT008	0287 94V 1006	200.33			
PT009	RHI 0083 RGI-0712	228.00			
PT010	1614521-1 REVJI	184.41			
PT011	20550-001	199.52			
PT012	6493879 NI	197.78			
PT013	PNI 28010-41	86.22			
PT014	435-0001-04	135.23			
PT015	LIA 3307	129.05			
PT016	6370942 620 01	198.16			
PT017	6370942 620 01	195.77			
PT018	6370942 620 01	196.38			
PT019	API-0009PCB1	926.36			

Figure 3-13. Example of Inventory Control Sheet used to track the Pantex circuit boards.

alumina tubes. This was done in an effort to protect the air traps from direct contact with the metal interconnect and exhaust tube, which become warm during processing. The alumina tubes with the air traps inside, were placed in the gas sampling ports. Also, to prevent contamination of the air traps from emissions that escaped from the microwaves or conventional furnace, Tygon tubing was attached to the end of the alumina tube that was exposed to the fume hood. The tubing was then run to the in-house vacuum system and the vacuum system was turned on to a preset low level. In most cases, the off-gas unit was at temperature when the processing began. The exceptions were for the microwave off-gas tests conducted at 400°C. For these, a range of temperatures was used because it was not possible to keep the microwave off-gas unit at 400°C for the entire 15 minutes of processing (temperature continued to rapidly increase) without deactivating the magnetron. The equipment and supplies used in the study are shown in Table 3-8.

The original experimental plan consisted of a series of 18 experiments (see Figure 3-14 and Table 3-9), and each was to be repeated 2 times. However, after reviewing the results from the toluene study and data from the microwave off-gas tests, a number of tests were eliminated from the conventional heating portion of the experiment. Those eliminated are indicated with an asterix (*) in Table 3-9. Other tests in the conventional heating study were only run once.

The conventional off-gas unit consisted of a Thermolyne tube furnace lined with an alumina tube (see Figure 3-15). In order to simulate conditions that existed in the microwave off-gas unit, SiC filters and phosphate-bonded filters were positioned within the tube to provide the same bed length as was found in the microwave system. Periodically between

Table 3-8. Equipment/Materials Used in Single Gas and Pantex Feed Parametric Studies and Vitrification/Metal Recovery Experiments.

Microwave Ovens:	Goldstar Multiwave Model #MA1164M (combustion chamber) Goldstar Multiwave Model #MA1280M (off-gas chamber)
Temperature Display:	Omega DP460-TC (off-gas chamber)
Temperature Controller:	Omega CN9120A (combustion chamber)
Thermocouple:	Omega Inconel-Shielded XCIB-K-1-4-3 (K-type)
Air Traps:	OI Analytical, College Station, TX 6mm x 4.5in, Tenax-TA Part # 260216
Flowmeter:	Dwyer Instruments, Inc., Michigan City, IN RMB-54-SSV Max. Pressure: 70psi, Max. Temp: 130°F
Reticulated Filters:	Selee Corp., Hendersonville, NC PBA: 25ppi x 2 in diam. SiC: 25ppi x 2in. diam.
Refractory Lining/Housings:	Thermal Ceramics, Augusta, GA Kaowool HS-45 Board Kaowool Blanket
Refractories/Susceptor Matl.	Rath Performance Fibers, Inc. Altra® KVS 17/400 36" x 24" x 1" Board 3" ID x 5" OD KVS 17/400 cylinder
Conventional Furnace:	Thermolyne Tube Furnace, Model F21135 12" long chamber with a 2" diameter 120V, 1350W, 11.25 amps Max. Temp. 1200°C Fisher Scientific - Norcross, GA
Syringe:	Hamilton Syringe 1000µl gas-tight syringe, #81343 Reno, NV
Toluene:	NOAH Technologies Corp. 7001 Fairground Pkwy. San Antonio, TX 78238 Purified grade Toluene CAS 108-883

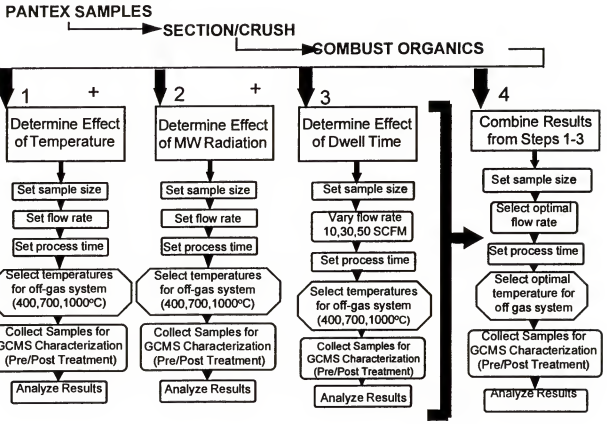


Figure 3-14. Flowchart for the full-factorial parametric experimental plan.

Table 3-9. Parametric Study Matrix Using Pantex Feed Material.

Microwave		Conventional	
Temperature (°C)	Flow Rate (SCFM)	Temperature (°C)	Flow Rate (SCFM)
1000	10	1000	10
1000	30	1000	30
1000	50	1000	50
700	10	700	10
700	30	700*	30
700	50	700	50
400	10	400	10
400	30	400*	30
400	50	400	50

Total number of trials = 18
Total number of repeats = 2
Total number of experiments = 36
Air traps required = 72

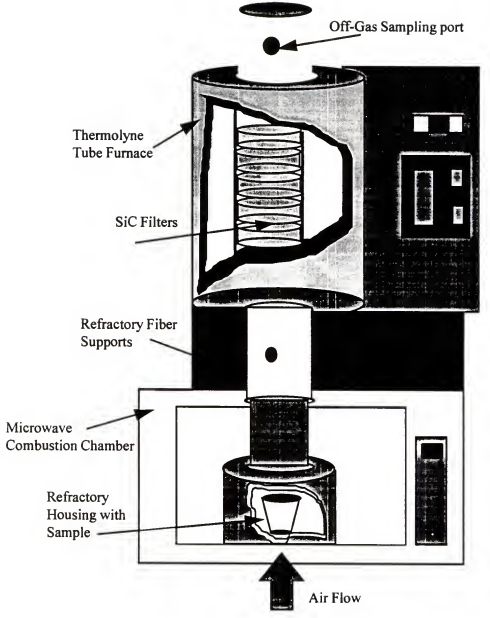


Figure 3-15. Schematic representation of conventional off-gas system.

runs, both systems were cleaned using compressed air. This was done to ensure adequate air flow through the system and prevent build-up of particulates that was found to occur at lower operating temperatures (both microwave and conventional systems).

Pantex Feed - Vitrification/Metal Recovery

Even though the Pantex feed material consisted of a wide variety of circuit boards, it was decided that it would be beneficial to determine the metal content of a single board to get an estimate of the amount and types of metals that could be recovered from a single board. In addition, tests were to be conducted to determine the composition of the glass created during the process and if any of the precious metals were encapsulated within the glass.

Board #PT101 was selected for this experiment. After sectioning and crushing the weight of the board was approximately 787g. The board was processed in batches, where each batch weighed approximately 70 to 100 grams and was processed for 30 minutes in the Goldstar microwave (model #MA1164-M) to remove the organics from the circuitry. Following the initial removal of organics, the remaining ash was heated again for another 60 minutes to ensure all organics were removed prior to vitrification. The weight of the remaining ash was ~ 518g (% weight reduction ~34%).

Vitrification/metal recovery was carried out in the Raytheon microwave. A susceptor consisting of 4 plates of 30 wt% SiC and Alfrax cement were positioned inside the walls of a refractory housing made from the Rath Altra® KVS 17/400 board. An alumina crucible with the sample material was placed inside the susceptor, a cover with an opening for the optical pyrometer was placed on top. The assembly was then positioned in the Raytheon microwave

on top of 4 high temperature refractory bricks (see Figure 3-16). Position adjustments were made so the optical pyrometer was in line of sight with the sample material. Four magnetrons were used (1,3,5,7) for a total available power of 3200W. The initial duty cycle was set at 30%. After five minutes it was increased to 40% and was gradually increased up to 80% where it remained for approximately 20 minutes. After that, the pyrometer began controlling the output of the microwave and duty cycle remained at 100%. Processing temperature range was 1545-1550°C. Processing times for the 3 batches ranged from 68 (first batch) to 74 minutes. Processing time for the last two batches was increased slightly as the first batch did not appear completely vitrified and some small metal beads were found in the glassy material. Given an additional period of time, it was believed these beads would have settled to the bottom with the rest of the metal. This was found to be true for the second and third batch.

Characterization Techniques

Gas Chromatography/Mass Spectroscopy

Gas chromatography with mass spectroscopy (GCMS) is a technique that uses gas chromatography separation methods together with the detection capability of mass spectroscopy. For the analysis method to work, the material to be analyzed is vaporized by the GC unit and sequentially separated by flowing through a GC column. The column is usually a fused silica, metal or plastic tube packed with an adsorbent material or coated with a variety of materials specifically selected to allow separation of the various ions as they pass through the column in the inert carrier gas. However, in GCMS, a packed column cannot be used because mass spectrometers operate at low pressures (10^{-5} - 10^{-7} Torr) and cannot

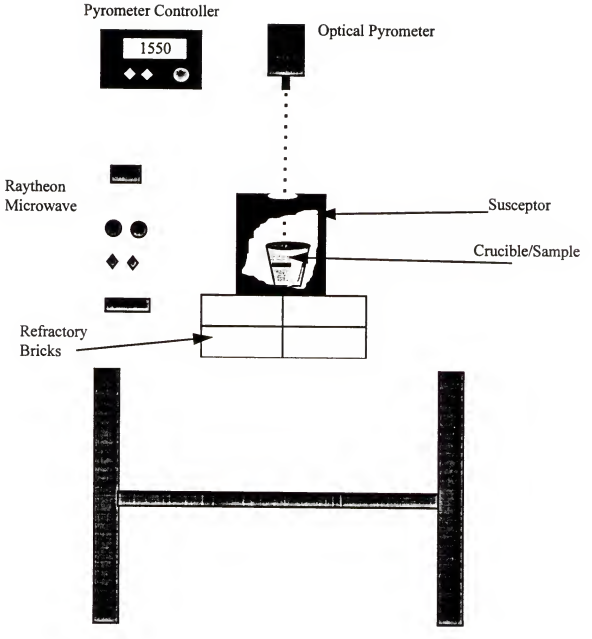


Figure 3-16. Schematic of vitrification/metal recovery set-up in Raytheon microwave.

manage the high volume of carrier gas required for a packed column. Various other interfaces were attempted through the years but were not considered efficient. Capillary GC tubes which use much lower carrier gas flow rates are currently used. The effluent from the chromatograph is directed through the transfer line to the ion source where it is ionized. The ions (or ion fragments) are detected by their respective masses. The chromatogram is a result of repeated scans of the mass analyzer and consists of the sum of all of the mass to charge ratio values (m/z) and the relative intensities of the ions [Gro95]. A simplified schematic of a GCMS unit is shown in Figure 3-17.

For this study, the Tenax air traps were thermally desorbed using an OI Analytical desorption unit (Model 4560). On the schematic, the desorption unit would be used to transport the sample to the detector rather than injecting the sample through the injection port. A Hewlett Packard 5890 gas chromatogram was used to separate the analytes using a DB-5 column, 30m, 0.32mm ID with a film thickness of 0.25μm (internal coating). The internal standards were spiked at concentrations of 250 ng/tube. The internal standards were difluorobenzene, toluene-d8 and bromofluorobenzene. The method used to calculate the concentration of the compounds detected is as follows. The internal standards are run and a response value which corresponds to the integrated area under the peak for that material is determined. The measured response for the standard is compared to responses generated for compounds with similar properties detected from the sample and a concentration is calculated as shown in the following equation:

$$\frac{response\ of\ standard}{concentration\ of\ standard} = \frac{response\ of\ sample}{X\ concentration\ of\ sample} \qquad 3.1$$

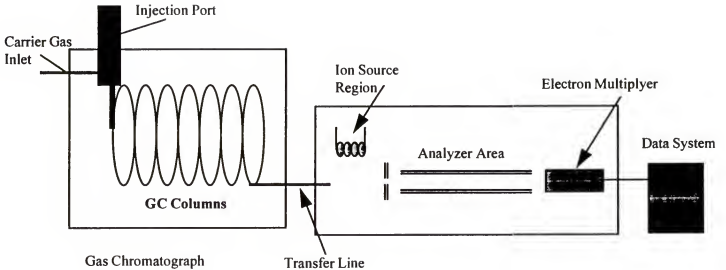


Figure 3-17. Simplified schematic of a typical GCMS system. Adapted from Grob [Gro95].

An example of the above calculation to determine the concentration of toluene from GCMS data is shown below: Given (GCMS characterization of air trap, sample PS-400-50-A2):

internal standard: toluene-d8 response: 516751 Conc: 250.00ng

target compound: toluene response: 65473315

$$\frac{516751}{250\ ng} = \frac{65473315}{X\ ng} = 31675ng = Concentration\ of\ Toluene \qquad 3.2$$

The actual amount of toluene as reported by computer analysis of the responses was slightly less, with a value of 31670.23. The difference is most likely due to rounding off errors.

Metal and Glass Characterization

Glass and metal samples from vitrification/metal recovery #2 were submitted for characterization. The metal was analyzed using standard x-ray fluorescence (XRF) methods and the glass was analyzed using inductively coupled plasma spectroscopy (ICP).

Glass characterization was carried out using inductively coupled plasma spectroscopy (ICP). In general, ICP analysis is conducted by pumping an aliquot of liquid into the system. The liquid is vaporized and the vapor is exposed to a plasma operating at approximately 7000K. The atoms are excited to an elevated energy state, and upon returning to ground state emit characteristic radiation. As each element has a specific emission pattern, it is possible to use spectroscopy methods (either mass or electron) to determine the element, and to compare the intensities of the lines to known standards, thus determining the concentration of the elements [Cla91].

The glass samples presented for characterization were dissolved using two dissolution techniques. The first involved adding 2.5 g of sodium hydroxide (fluxing agent) to approximately 0.25g of glass and heating to 725 °C in a nickel crucible. After heating, the residue was dissolved in a mixture of nitric acid and water. A second dissolution using cesium hydroxide was carried out to allow determination of sodium. The two liquid samples were further diluted to achieve a final volume of 250ml. Calibration standards for each element were introduced at 3 concentrations (1, 5 and 10 mg/l (ppm)).

The metal samples were examined using XRF. In this technique, the sample is exposed to x-rays. The radiation causes the sample to emit characteristic fluorescent radiation which can then be analyzed using spectroscopy methods.

CHAPTER 4
MICROWAVE/MATERIALS INTERACTIONS

Qualitative Discussion

Microwaves are electromagnetic waves with wavelengths ranging from one meter to less than a millimeter in length. The corresponding frequencies range from 300 megahertz (MHZ) to 300 gigahertz (GHz) [Met83]. Not all materials respond to microwave energy in the same manner. Some materials are transparent to microwave energy, while others absorb or partially absorb the energy (Figure 4-1). Materials that absorb or partially absorb microwave energy, convert it to heat. The efficiency of the process is dependent on the material's dielectric and magnetic properties, as well as the composition and structure of the phases present [Tin88, Sut89]. The degree of interaction is related to the material's complex permittivity, ϵ^* (F/m), which is composed of a real part, the dielectric constant, ϵ', and an imaginary part, the dielectric loss factor, ϵ''. The relationship is described in the following equation [Sut89]:

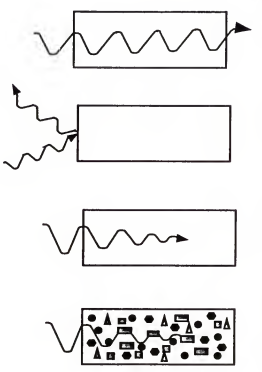
$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon_0(\epsilon_r' - j\epsilon_{eff}'') \qquad 4.1$$

where:

ϵ_0 = permittivity of free space (8.86×10^{-12} F/m),

ϵ_r' = relative dielectric constant (ϵ'/ϵ_0) and

ϵ''_{eff} = effective relative dielectric loss factor ($j = (-1)^{0.5}$).



MATERIAL TYPE	TYPICAL MATERIAL	PENETRATION
Transparent (low loss insulator)	Pure alumina, silica	Total
Opaque (conductor)	Aluminum, steel	Negligible (reflected)
Single Phase Absorber (lossy insulator)	Silicon carbide, iron oxide Pure gases	Partial to Total
Mixed Phase Absorber Transparent/Conductor/ Absorber (mixed) matrix = low loss particulates: ● = opaque (reflector) ▬ = absorber	Silica/copper/SiC Mixed gases	Partial to Total

Figure 4-1. Basic microwave/material interactions. Adapted from Sutton [Sut89].

The real part of ϵ^*, the dielectric constant (ϵ'), is a measure of the amount of electrical charge a material can store when exposed to a electric field. It is a comparative ratio of the electric field strength in a vacuum (perfect dielectric) to the electric field strength in the material [Wea86]. A "good" dielectric material has a small dielectric constant and absorption is minimized. The imaginary portion of ϵ^*, ϵ'', or the dielectric loss factor, describes the losses exhibited by the material. The dielectric loss factor is the principal factor in determining the conversion rate of electrical energy into thermal energy in the sample prior to phase transition losses [Che93a,b,c]. As heat is generated internally, power dissipation remains independent of heat flow through the surface until convection or conduction losses become significant. This is in direct contrast to conventional heating methods which are dependent on the thermal conductivity of the medium being heated.

It has been generally accepted that as the microwaves enter the material, internal electric fields are generated. These fields induce translational motions of free or bound charges (electrons or ions) and rotate charge complexes (i.e., dipoles). Resistance to these motions from inertial, frictional or elastic forces cause losses and attenuate the electric field within the material.

Altering the applied frequency has varying effects on the dielectric constant and loss factor. As shown in Figure 4-2, at low frequencies, the loss factor is small while the dielectric constant remains at its maximum value because the dipoloes have sufficient time to follow the variations of the applied field (Region I) and store the energy supplied by the external source. As frequency increases (Region II), the dipoles continue to match oscillation variations with the applied field until they are vibrating in resonance with field

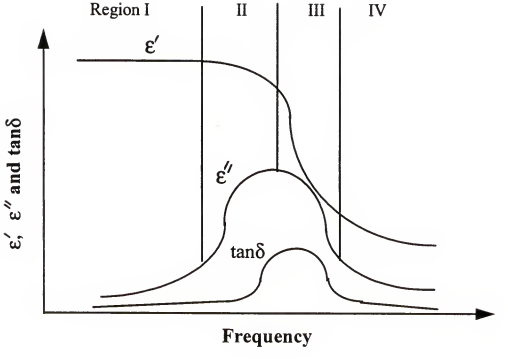


Figure 4-2. Dielectric constant, loss factor and loss tangent as a function of frequency. Adapted from Metaxas and Meredith [Met83].

at the maxima of the loss factor peak. As the frequency advances past this point into Region III, it becomes increasingly difficult for the dipole rotations to keep up with the applied field. This is supported by the decrease in the value of both the dielectric constant and the effective loss factor. In Region IV, the applied frequency is so high that the dipole oscillations can no longer respond (the material becomes "transparent" to the frequency). As a result, the dielectric constant and loss factor are very small [Met83].

Microwave heating is thought be a result of polarization and conduction losses in a dielectric material. The behavior exhibited by the material shown in Figure 4-2, was an example of the effects of frequency on dipole polarization mechanisms. A brief discussion of the various polarization mechanisms (see Figure 4-3), including the mechanisms believed to be most relevant to microwave heating is contained within this section. Electronic polarization involves the shift of the valence electron cloud within the material with respect to the nucleus and occurs at very high frequencies (10^{15} Hz). Atomic or ionic polarization is the displacement of positive and negative ions within a material and occurs at frequencies that are too high to couple directly with microwave energy (10^{12} - 10^{13} Hz). Interfacial or space charge polarization occurs when charges build up at a barrier and create localized polarization in the material (10^{-3} - 10^{3} Hz)). Orientation or dipolar polarization occurs in the sub-infrared region (10^{-3}-10^{11}Hz) and is the disturbance in the thermal motion of the dipoles producing a net orientation in the direction of the applied field [Kin76, Hen90]. There are two orientation polarization mechanisms. In the first mechanism, oscillation of the permanent dipoles around an equilibrium position occurs (vibration losses). The second mechanism involves the rotation of dipoles between equivalent equilibrium positions over

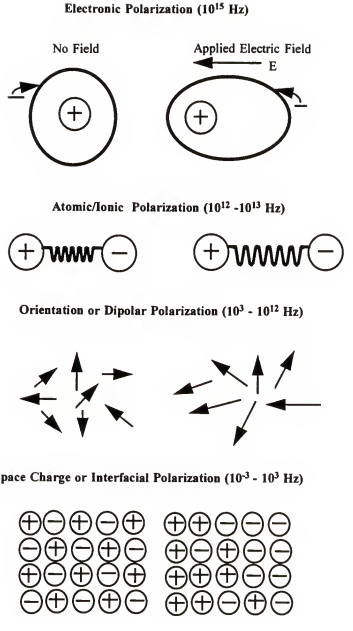

Electronic Polarization (10^{15} Hz)
No Field
Applied Electric Field
E
Atomic/Ionic Polarization (10^{12} -10^{13} Hz)
Orientation or Dipolar Polarization (10^{3} - 10^{12} Hz)
Space Charge or Interfacial Polarization (10^{-3} - 10^{3} Hz)

Figure 4-3. Schematic illustration of the four polarization mechanisms. Adapted from Von Hippel, Kingery and Uhlman, and Hench and West [Von 54, Kin76, Hen90].

atomic distances and is often referred to as a relaxation loss. At low frequencies, the ions jump easily with the changing electric field, however, as the frequency increases the ions cannot keep up with the shifts and a lower dielectric loss is observed.

There are two other loss mechanisms; conduction and deformation losses. Conduction losses are similar to relaxation losses, however, they result from ionic transport over longer distances and are dependent on dc conductivity. Deformation losses occur in some materials (i.e., glasses) at very high frequencies due to high frequency orientation polarization.

Since each polarization mechanism is independent of the other, the effect of all polarization mechanisms, or the total polarizability (α_{tot}) in a dielectric material can be represented as follows [Von54, Kin76]:

$$\alpha_{tot} = \alpha_e + \alpha_a + \alpha_d + \alpha_s \qquad 4.2$$

where the subscripts e,a, d, and s represent the contributions from electronic, atomic, dipole and space charge polarization mechanisms, respectively [Kin76]. Similarly, each of the above described mechanisms has an effect on the behavior of a dielectric material when exposed to an applied field. In addition there may be contributions from conduction losses that cannot be separated from the polarization losses during dielectric measurement techniques. Therefore, one can define the effective loss factor as the sum of all loss contributions[Met83]:

$$\epsilon''_{eff} = \epsilon''_{e} + \epsilon''_{a} + \epsilon''_{d} + \epsilon''_{s} + \frac{\sigma}{2\pi f \epsilon_0} = \frac{\sigma_{eff}}{2\pi f \epsilon_0} \qquad 4.3$$

where:

σ = conductivity due to conduction losses

σ_{eff} = total effective conductivity (S/m),

ϵ_0 = permittivity of free space (8.86×10^{-12} F/m),

f = microwave frequency (GHz).

Quantitative Discussion

The ratio of the dielectric constant to the loss factor is referred to as the loss tangent or dissipation factor, tanδ. The loss tangent is also defined as the ratio of the loss current to the charging current [Fat94, Sut89, Met83].

$$\tan\delta = \frac{\epsilon''}{\epsilon'} = \frac{\epsilon''_{eff}}{\epsilon'_{r}} = \frac{\sigma_{eff}}{2\pi f \epsilon_0 \epsilon'_{r}} \qquad 4.4$$

The loss tangent is frequently used to describe material losses and to provide an indication of how well the substance interacts with the microwave field.

Microwave transparent materials have low values of tanδ (~ 0.01 for pure alumina at room temperature and frequencies between 1-3GHz [Bat95]) while materials that readily absorb microwave energy have high values (~ 1.25 for silicon carbide at room temperature and frequencies between 1-3GHz [Bat95]) over a wide range of temperatures and frequencies). Water has a loss tangent of approximately 0.157 at room temperature and a

frequency of 3GHz [Von54]. It should also be noted that the value of tanδ is dependent on the microwave frequency and temperature.

According to several studies, dielectric losses in both glasses and polymers are temperature dependent [Hen90, Che93a, Lew93, Wei95]. As the temperature in increased, the speed at which the molecules vibrate is also increased. Because the molecules' natural vibration is increased and approaches that of the applied frequency, they are able to couple in with higher frequencies, thus shifting the absorption peaks to the higher frequencies. Thus, the frequency at which the maximum tanδ occurs, $f_m(\tan\delta)$, shifts to higher frequencies as shown in Figure 4-4. The relationship between f_m and temperature is demonstrated in the following equation [Hen90]:

$$f_m = f_0\left(\frac{\epsilon_s}{\epsilon_\infty}\right)^{1/2} \exp\left[-\frac{E_a}{kT}\right] \qquad 4.5$$

where:

ϵ_s = relaxed static dielectric constant

ϵ_∞ = unrelaxed high-frequency dielectric constant

f_0 = dipole frequency of oscillation (10^{12} to 10^{13} sec^{-1})

k = Boltzman's constant 1.38 x 10^{-23} J/°K

T = temperature (°K)

E_a = activation energy

At a given frequency of radiation, as temperature increases from an external source, or self-heats from microwave energy, tanδ rises slowly until a critical temperature, T_C, is reached (see Figures 4-5 and 4-6). The loss tangent continues to rise (as the applied or self-

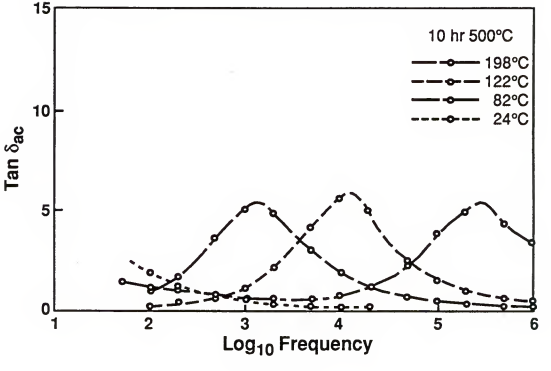


Figure 4-4. Dielectric loss peak shift due to increasing temperatures for $Li_2O{\bullet}2SiO_2$ glasses. Adapted from Hench and West [Hen90].

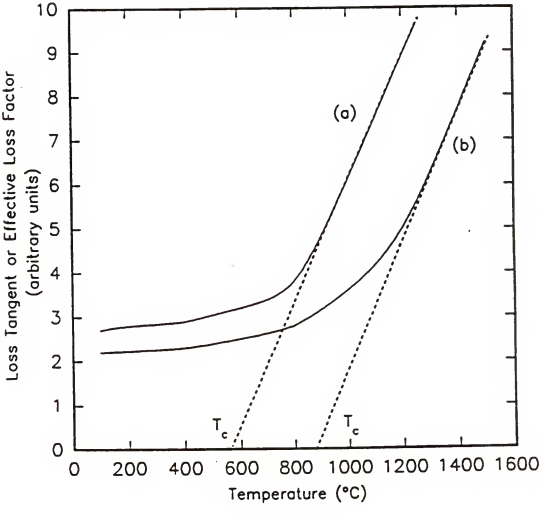
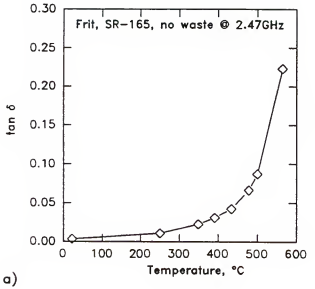
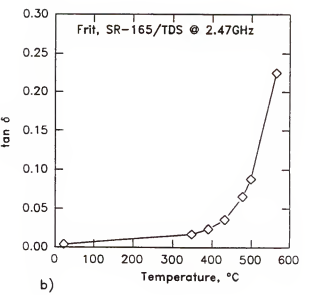


Figure 4-5. Loss tangent versus temperature for typical ceramics. a) Low loss with microwave absorbing additives; b) ceramic with no additives. Adapted from Moore [Moo93].



a)



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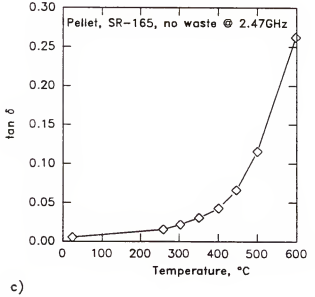

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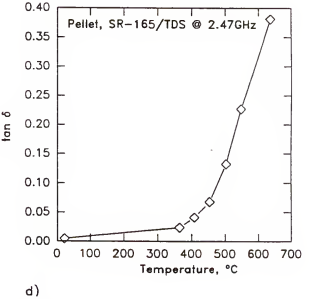


d)

Figure 4-6. Tanδ versus temperature for both glasses (pellet and frit) at ~ 2.45GHz [Sch94b].

heating temperature increases), microwave energy is absorbed more efficiently and thus, the temperature increases at an even greater rate. If uncontrolled, this process could continue and cause thermal runaway, an exponential increase in temperature [Fat94, Met83].

A quantitative term often used in describing microwave/material behavior is the amount of power absorbed per unit volume. An approximation of this term, P (W/m^3), is given by [Sut89]

$$P = \sigma |E_{rms}|^2 = 2\pi f \epsilon_0 \epsilon'' |E_{rms}|^2 \qquad 4.6$$

where:

E_{rms} = root-mean squared value of the internal field (V/m).

This equation provides only an approximation of the power absorbed, as it is assumed that the power absorbed is uniform throughout the sample and that thermal equilibrium has been achieved. Other factors, such as the magnitude and uniformity of the applied electric field, sample geometry, size, location within the cavity and type of cavity also have an effect on the internal electric field (E) and thus, a direct effect on the power absorbed. The electric field inside a typical multimode microwave oven used for sintering operations is about 10^5 to 10^6 V/m [Fre93] and may vary considerably with sample position within the cavity, the size of the cavity and load. Mode stirrers are often used to provide a more uniform electric field within the cavity. Turntables are also used to assist in uniform heating. However, rather

than perturbing the electric field, as with mode stirrers, they rotate the material within the cavity. This action exposes the sample to the various resonant modes found in multi-mode ovens in a cyclic manner, decreasing the occurrence of "hotspots."

From the above equations and calorimetric data, it is possible to determine an approximate heating rate formula [Met83, Sut89]:

$$\frac{T - T_0}{t} = \frac{0.556 \times 10^{-10} \epsilon''_{eff} f E^2_{rms}}{\rho_b C_p} \quad °C/\text{sec} \qquad 4.7$$

where:

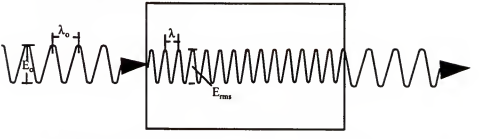
ρ_b = bulk density (g/cm^3)

C_p = specific heat (cal/mole°C)

The only term in equation 4.7 that is not easily measured experimentally is E_{rms}. Therefore, this equation may be used to calculate the root-mean square of the electric field, and that value used in equation 4.6 to determine the power absorbed per unit volume.

As was shown in Figure 4-1, microwaves interact with materials in different manners. A microwave transparent material absorbs no energy from the electromagnetic waves as they passes through the object. When the microwave encounters the surface of the material, its velocity and wavelength are altered in much the same way as light as it passes through a transparent object, as index of refraction (n), and the relative dielectric constant (ϵ'_r), are related ($\epsilon'_r = n^2$, if absorption is zero) [Von54, Kin76]. The relationships that shows how the electric field is altered when it enters a microwave transparent material is shown in Figure 4-7 and by the following relationship [Joh93]:

A. Transparent Material



at f = 2.45GHz = 2.45 x 10^9 Hz
λ_o = 12.2 cm = 0.122m
c = velocity of light = 2.989 x 10^8 m/s

$\lambda f = v$
0.122m (2.45 x 10^9 Hz) = v
v = 2.989 x 10^8 m/sec

since $\varepsilon_r' = n^2$
and n = v/c
then $(\varepsilon_r')^{1/2} = v/c$

assume $\varepsilon_r' = 4$
then v = 1.495 x 10^8 m/s

if v = 1.495 x 10^8 m/s
then λ = 0.061 m = 6.1 cm

And from Equation 4.8:

$$E_{rms} = E_o/\varepsilon_r'$$

$$E_{rms} = 10^6/2$$

$$E_{rms} = 5 \times 10^5 \text{ V/m}$$

B. Absorbing Material - Equation 4.9

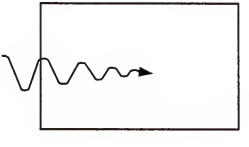


Figure 4-7. Schematic illustration of the behavior of a dielectric as; A) an electric field passes through a microwave transparent material; B) a microwave adsorbing material.

$$E_{rms} = \frac{E_0}{\epsilon_r'} \qquad 4.8$$

If the material is capable of interacting with the electromagnetic wave through one or more of the mechanisms described above, then energy from the electric field is decreased as it is absorbed by the material. The equations that illustrate how the electric field decreases as the microwaves enter and pass through a material are given below [Met83]:

$$E = E_{max}(e^{-\alpha z})(e^{j(\omega t - \beta z)} \qquad 4.9$$

where:

E_{max} = maximum electric field strength

α = attenuation factor,

ß = phase factor,

z = direction of applied energy and,

$$E \propto e^{-\alpha z} \qquad 4.10$$

where:

α = $1/2D_p$, the penetration depth, giving:

$$E \propto e^{(-\frac{1}{2D_p}z)} \qquad 4.11$$

Thus, while E in the cavity may be 10^5 to 10^6 V/m, the E_{rms} internal may be considerably smaller (depending on the penetration depth) if the attenuation is high. Earl has shown for water inside a 500W microwave, E_{rms} is less than 10^3 V/m [Ear94].

It is often beneficial to calculate the depth of penetration, D_p, a term that describes the location where the incident power is reduced by 1/e from its value at the surface [Met83]:

$$D_p = \frac{\lambda_0}{2\pi(2\epsilon_r')^{1/2}} \cdot [(1 + (\epsilon_{eff}''/\epsilon_r')^2)^{1/2} - 1]^{-1/2} \qquad 4.12$$

where:

λ_0 = incident wavelength.

The depth of penetration increases with increasing wavelengths (lower frequencies). If the penetration depth is greater than or within the range of the sample dimensions, volumetric heating will result and uniform processing is possible. However, if D_p is much smaller than the sample, surface heating occurs and results in a non-uniform heat distribution similar to conventional (radiant) heating [Fat94].

CHAPTER 5
RESULTS AND DISCUSSION

Introduction

The initial objectives of the work with electronic circuitry were to "destroy beyond all recognition" any components presented for treatment, achieve a significant volume reduction to facilitate storage, and encapsulation of any remaining materials that may be hazardous to the environment. All of the initial objectives of the project were achieved. During the course of the project, it was recognized that the metals contained on the boards could be recovered and made available for resale. It was also speculated that if the glass material produced was chemically stable, it could be recycled into other products.

In order to proceed with the project in a responsible manner, a method to remediate the volatile organic species emitted during treatment had to be included in the processing regime. Various types of electronic circuitry were presented for pyrolysis, vitrification and metal recovery experiments. These included two different types of circuit boards obtained from WSRC, defense-related circuitry (trajectory switches, firesets and Pantex circuitry) and commercial transistors. A summary of the results from the processing regimes on the various categories of circuitry is provided in the following sections.

Primary Wastes

WSRC Circuit Boards

Among the first circuit boards processed were two identical boards designated as 2-06 and 2-07 received from WSRC. When preparing the boards for processing, it was observed that the boards did not appear to be reinforced with glass fiber mats. Literature research indicated that it was likely these boards were reinforced with paper [Har94]. The 2-07 sample board was reduced to ash in approximately 84.5 minutes (in stages) using an 800W, 2.45GHz Goldstar microwave. After microwave processing, weight reductions in the range of 30-50% and volume reductions in the range of 50-80% following removal of organics were observed. A summary of results for these two circuit boards is shown in Table 5-1. While significant volume and weight reductions were achieved for this type of circuitry, there was insufficient silica content in the boards to achieve a vitreous solid without adding glass formers. After processing, the appearance of the 2-07 sample was a black, volcanic mass with some phases that appeared to be partially vitrified. Spheroidal metallic spheres were found throughout the glassy sample and were easily recovered.

Similar processing was carried out on the board designated as 2-06. After initial processing (removal of organics and attempting vitrification without additives), a portion of the 2-06 board (67.45g), was mixed with SR-165 frit (see Table 2-3) [Sch91]. The frit was incrementally added to the sample until a vitreous solid was achieved. Upon removal from the crucible, it was observed that a large magnetic metallic spheroid had settled to the bottom of the melt. This metal was easily removed from the glass product. As both these tests were scouting runs to determine feasibility of microwave processing for this wasteform,

Table 5-1.Processing Summary For Circuit Boards Obtained from WSRC [Sch94b].

Sample ID	Initial/Final Wt (g)	%Wt Decrease	Initial/Final Vol. (cm^3)	Process Time (min)	Power (W)	T_{max} (°C)
2-07	126.2/69.58	44.9	~146/27	126.5	800-3200	1415
2-06	127.67/67.45	47.2	--	121	800-3200	1449
2-06*	67.45/107.95	--	--	83	3200	1449

* Glass frit was added to this run in order to obtain a vitreous mass

characterization was not conducted on these products. However, the success of the treatment provided the impetus for further research with similar materials.

Commercial Tungsten-Based Transistors

Several commercial tungsten-based transistors were obtained for microwave destruction. The scanning electron micrographs with accompanying energy dispersive spectra (SEM/EDS) analyses of these samples showed they consisted primarily of tungsten, along with quantities of gold, copper and silica (Figure 5-1). The crushed transistors were placed in a crucible, mixed with SR-165 frit, positioned within the susceptor and processed for 15 minutes in the Raytheon microwave. The maximum temperature achieved was 1478°C, not nearly sufficient to melt the tungsten, which has a melting temperature of 3410°C [Sch93a]. A vitreous mass was obtained, and destruction of the ceramic/wire portion of the transistor was achieved (Figure 5-2).

Glass Mat Reinforced Circuit Boards

In this study, reinforced printed circuit boards recovered from various pieces of computer equipment were used. The processing results for a 286 motherboard are shown in Table 5-2. As can be seen from these data, the samples lost approximately 30% of their original weight as a result of decomposition of the organic phases, and that approximately 30% of the original weight consisted of metal components that were recovered after vitrification. The samples that attained the most desirable form (completely vitreous with complete metal separation) were those that had been ramped incrementally up to the processing temperature by adjusting the duty cycle.

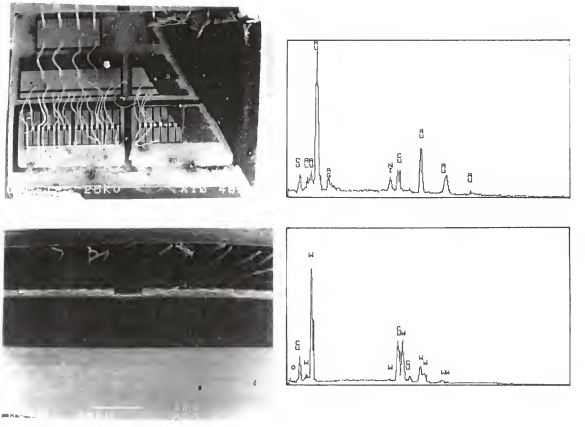


Figure 5-1. Scanning electron micrograph with corresponding EDS spectra for the commercial transistors. a) Top view with protective cover removed revealing gold wire circuitry; b) cross-section of transistor revealing tungsten base.

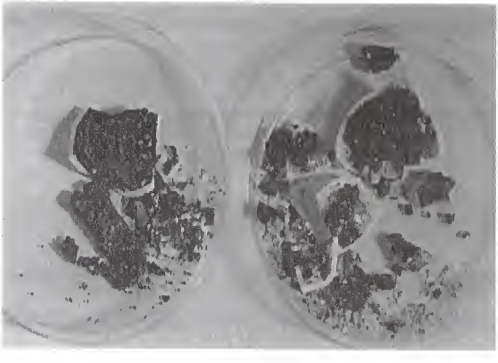


Figure 5-2. Photograph of tungsten transistor after microwave processing.

Table 5-2. Processing Results for Metal Recovery Experiments from the 286 Motherboard [Sch94].

Sample ID	Initial/Final Wt (g)	Time (min) 900W	% Wt Loss	Time (min) (800-3200W)	T_{max} (°C)	Wt of metal recov'd (g)	% of Metal/Sample
286/1	88.1/58.7	50	33.3	39.9	1450	26.2	29.7
286/2	86.4/59.9	30	30.7	47	1460	25.3	29.3
296/3	76.7/53.3	40	30.5	48	1460	22.4	29.3

Firesets and Trajectory Switches

Firesets

Five samples of a crushed, black material were received from WSRC. These samples were what remained of five unclassified electronic components referred to as firesets. Vitrification had been attempted by WSRC staff, but was not possible in available equipment. Therefore, microwave processing was conducted at UF. A portion of sample 2-79385 was placed in a 800W microwave located in the fume hood to test for emission of volatiles. As no smoke or fumes were observed and high temperatures were necessary to achieve vitrification, all subsequent experiments were carried out in the Raytheon unit (maximum power used for these experiments was 4000W). The material interacted well with the microwave energy and no susceptor material was necessary to achieve temperatures in excess of 1300°C. However, susceptors were used in three of the runs in an attempt to further increase processing temperatures and to help maintain the integrity of the crucibles (the susceptors provided additional insulation to slow the cooling process). On several occasions, the process was observed through the optical pyrometer. During these visual examinations, the sample appeared as a bubbling mass with sporadic arcing. When temperatures exceeded 1500°C, a green-colored plume arising from the sample was observed via the observation port. Several times the crucibles cracked either during processing or as the sample cooled. This was thought to be due to rapid changes in temperature causing failure due to thermal shock. The resulting material for all five samples was a solid black mass. The sample processed at the highest temperatures (2-

79388) appeared somewhat more vitreous than the other samples, and small metallic beads were observed around the edge of the crucible. No glass frit additives were necessary to achieve the semi-vitreous state. Processing temperatures, times and observations are shown in Table 5-3. All samples were returned to WSRC for leach testing. Although the data from leach testing was not made available, the end results reported by WSRC indicate that the microwave processed samples met EPA leach test standards [Wic95].

Trajectory switches

Portions of the as-received crushed ceramic-like material were placed in an alumina crucible and positioned inside the 800W microwave. Within five minutes the thermocouple registered a temperature of 1189°C. Flames were observed after only several minutes of processing. The run was interrupted several times during the initial run to check the integrity of the crucible and additional sample material was added after 8 minutes of processing (the polymeric material had pyrolyzed, and volume reduction had occurred so it was decided to add more sample, total initial weight = 105.1g). The sample was processed a total of 30.5 minutes in the 800W microwave with a final temperature reading of 1217°C. After cooling, the sample was re-weighed (93.92g) and transferred to a new alumina crucible, positioned in the susceptor and the Raytheon microwave unit to further heat the sample. Four magnetrons were activated (3200W maximum power) and the optical pyrometer was used to monitor the temperature. After processing a total of 30.7 minutes with a maximum temperature of 1510°C, the sample did not appear vitreous,

Table 5-3. Results of Microwave Processing of Firesets Supplied by WSRC.

Sample ID	Total Process Time (min)	Susceptor Time (min)	Maximum Power (W)	T_{max} (°C)	Final Appearance
2-79383	40	15	2400	1489	volcanic-glass
2-79385	61.3	18.4	4000	1370	volcanic-glass
2-79386	47	--	2400	1348	volcanic-glass
2-79387	18	--	3200	1360	volcanic-glass crucible broke, some sample flowed out
2-79388	57.5	57.5	3200	1543	glassy, metallic beads on surface edges

although some melting had occurred. A portion of this sample was retained and sent to WSRC for analyses, while the remainder was subjected to further testing at UF.

As the material appeared to be ceramic in nature, and the researchers were not authorized to run any analysis on the samples, it was speculated that perhaps the addition of glass frit may break down or at least encapsulate the material. It was further decided that breaking up the material into smaller pieces may also increase interaction with the microwave energy (better volumetric heating with increased surface area [Dé90, Moo93]) so the sample was passed through the Braun chipper three times. Glass frit was added (SR-165; 37.94g, 50% of the weight of the sample to be processed). After 28 minutes of processing (20 minutes at the selected temperature range 1490-1510°C), the material appeared as a black vitreous solid mass. Upon removal from the crucible, small metallic spheroids were observed at the bottom of the melt. Some of the spheroids were gold/copper in color while others were silver in color. The sample was returned to WSRC for analyses. Summaries of the processing regimes are shown in Tables 5-4 and 5-5.

Initial Metal Recovery/Analyses

An experiment was conducted to determine the composition of the various metals contained within a computer circuit board as well as two of the commercial transistors. After removal of organics in the 800W microwave and processing at temperatures (1100-1150°C) selected to melt the gold (T_m Au = 1064°C) in the Raytheon microwave, metallic specimens were recovered using both magnetic and mechanical separation techniques. These spheres were then subjected to SEM/EDS analyses. The results are summarized in

Table 5-4. Microwave Processing of Trajectory Switch Without Glass Additives.

Sample ID	Initial Wt (g)	Final Wt (g)	Total Proc. Time (min)	Susceptor Time (min)	Power (W)	Tmax (°C)
TS1	105.1	93.92	61.2	30.7	800-3200	1510

Table 5-5. Microwave Processing of Trajectory Switch With Glass Additives (SR-165).

Sample ID	Initial Wt (g)	Frit Wt (g)	Total Proc. Time (min)	Susceptor Time (min)	Power (W)	Tmax (°C)
TS1F	75.86	37.94	28	28	3200	1508

Table 5-6. Metals Detected with SEM/EDS Analyses Conducted on Recovered Metal Spheroids [Sch93b].

Sample Type	Metals Detected
Spheroids Separated Magnetically	Fe, Sn, Pb, Al, Cu, Ti, Ni, Mn, Au, Si
Spheroids Separated Mechanically	Au, Ag, Cu, Sn, Al, Ni, Pb, Fe, Zn, Si

Table 5-6. Additional analyses of the metals contained in other circuit boards (Pantex feed) are described in the following section.

Vitrification/Metal Recovery

The processing results from the vitrification/metal recovery study after the organics were removed are summarized in Table 5-7. The samples were processed in the Raytheon microwave using 4 magnetrons (3200W) and the Capintec optical pyrometer to maintain the process temperature (1550°C) and control the duty cycle of the microwave.

Results from ICP analyses on the glass sample (from run #2) and XRF analyses on the metal are shown in Table 5-8 and Table 5-9 respectively. As can be seen from the data shown in Table 5-8, some of the elements that would be of concern in landfill disposal (As, Be, Cd) are found encapsulated within the glass matrix. Leaching experiments are necessary to determine the chemical durability of the glass product. The high content of alumina may be a result of processing in an alumina crucible together with amounts from ceramic substrates found in the surface mount components on the board. The low silica content is unexpected, and remains unexplained.

The composition of the amalgam metal pieces is as expected. High amounts of copper from connectors and foil interlayers, small amounts of gold and silver and a variety of other metals from wires, connectors, resistors and other board components. Calculating the net worth of one ton of similar circuit boards (estimated metal content = 27.7 wt%; avg. gold = 0.077wt%) and current gold prices ($292.50/oz as of 09/22/98) gives an estimated value of approximately $1950/ton. Contributions from recovery and resale of other metals was negligible when compared to the gold. If palladium and/or platinum were found in even very small amounts, the

Table 5-7. Processing Summary for the Vitrification/Metal Recovery Study.

Sample ID	Proc. Time (min)	Tmax (°C)	Wt Glass (g)	Wt Metal (g)	~ Vol. Red. (%)
Vit1	68	1552	52.8	75.23	~86%
Vit2	72	>1600	77.9	75.35	~84%
Vit3	74	1550	67.4	60.2	~86%
TOTAL	–	–	**198.1**	**210.78**	**85.3%** (avg)

Table 5-8. The Results of ICP Analyses on the Recovered Glass Sample (2 dissolution methods).

Element	Dissolution 1 (wt%) (CsOH dissolution)	Dissolution 2 (wt%) (NaOH dissolution)
Ag	<0.0021	0.0041
Al	17.7394	17.9566
As	<0.0632	<0.0242
B	0.8383	0.8296
Ba	0.4197	0.3793
Be	0.0185	0.0184
Ca	7.1271	6.7595
Cd	<0.0021	0.0056
Mg	0.3019	0.2789
Na	0.3998	--
P	0.0383	0.0273
Si	14.716	13.1234
Se	<0.4364	<0.1346

Table 5-9. Analysis of the Recovered Metal Using X-Ray Fluorescence (3 samples from Vit2). All amounts are in wt%.

ID	Cr	Mn	Fe	Ni	Cu	Pb	Au	Ag	Sn	Sb
1	0.93	0.30	9.08	1.38	77.61	1.84	0.058	0.23	8.27	0.27
2	0.18	0.05	3.14	1.47	79.65	3.53	0.14	0.27	10.79	0.54
3	4.49	2.31	18.27	2.46	64.28	1.92	0.033	0.208	5.49	0.41

reclamation value would substantially increase. These values provide only an indication of the current value of the metal and do not reflect expenditures involved in recovering or separating the precious metals from the ingot. However, as several companies are involved in this recovery operation using conventional smelting methods, it is assumed the value of the metals exceeds the cost of recovery.

Equipment and Secondary Waste

Off-Gas Systems

During combustion, the printed circuit boards emitted volatile and aromatic organic compounds as the polymeric portions were pyrolyzed. In early experiments, the gases were vented through the fume hood exhaust. However, this did not seem environmentally correct, and there was an interest in the composition of the gases being evolved. To remedy this problem, modifications were made to the 800W Goldstar microwave oven. These modifications were shown schematically in Figure 3-9. As mentioned earlier, this system was somewhat successful in preventing the release of a large portion of the emissions to the atmosphere. However, the available vacuum pump was not capable of pulling all the exhaust gases from the microwave and smoke/fumes leaked out through crevices in the microwave.

While the cold-finger apparatus may have been acceptable for lab practices, it did not appear to be readily amenable to scale-up operations. Scale-up to pilot plant and eventually commercial operations was of interest to the researchers and contract personnel, therefore, another off-gas system was designed. A literature survey provided information on other uses of microwave energy for treating emissions [Sci92, Che93, Mec91, Pro91]. Some of the described systems used microwave energy in combination with activated char or other media

to bring about a desired chemical reaction. It was decided that the microwave off-gas system designed for this program would use a bed of granulated SiC contained within a refractory cylinder. Silicon carbide was selected because it readily absorbs microwave energy and heats rapidly. A photograph of the system is shown in Figure 5-3. Over time, further modifications were made to the system and included adding phosphate-bonded reticulated alumina filters to provide additional insulation to connecting pieces, maintain the integrity of the filter bed by keeping the SiC particles in place and slowing air flow through the system. For some tests a HEPA filter was attached to the exhaust port to trap any gases/particulates that were not destroyed or decomposed in the off-gas treatment chamber.

While it appeared that the system functioned mechanically, testing of the emissions both before and after passing through the treatment bed was necessary to determine if the system was actually performing as expected. In order to conduct analyses on the emissions, a method for collecting the gas specimens had to be selected. The methods attempted and the final selection along with some data collected are discussed in later sections in this chapter.

As explained in the experimental section, that even though satisfactory results were obtained with the horizontal system, it was felt that the efficiency of the microwave off-gas system could be improved with additional modifications. These modifications included changing the geometry of the system, using two Goldstar Multiwave microwaves, and changing the filter bed from particulate SiC to SiC reticulated ceramic filters. These changes were shown schematically in Figure 3-11. A photograph of the working system is shown in Figure 5-4. Emission data obtained from this system is presented in later sections.

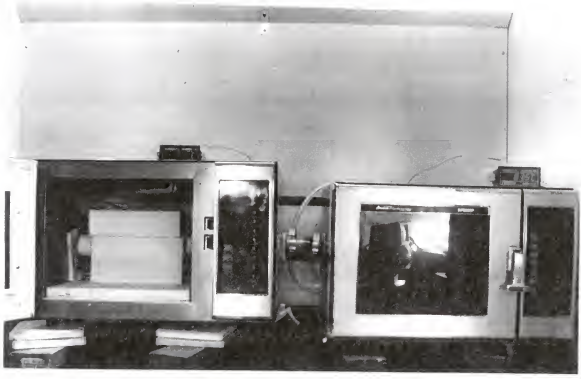


Figure 5-3. Photograph of horizontal microwave waste treatment system.

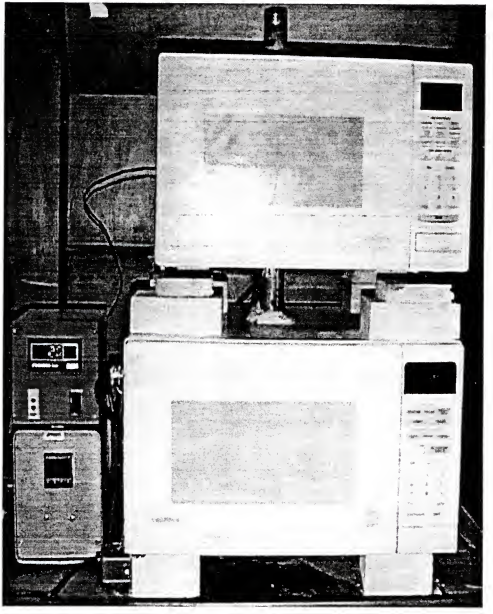


Figure 5-4. Photograph of the vertical microwave waste treatment system.

Gas Collection Methods

After constructing the horizontal microwave waste treatment system, experiments were conducted to determine a method for collecting gas specimens. Several techniques were tested. These included; gas syringes, Tedlar bags and Tenax air traps. Gas chromatography with mass spectroscopy (GCMS) analyses were performed on the gas specimens. Data from each method were analyzed for effectiveness, as was the practicality of using the various collection methods. The results are summarized in the following sections. Based on the data, and suggestions for sampling methods from the literature, a method was selected.

Gas syringe/Tedlar bag

Use of a syringe is one of the most common methods for introducing samples into the chromatograph. There are several different types of syringes currently in use, some for collecting and delivering liquid samples and those designed to collect and deliver gaseous samples. Luer-lock (50ml) gas tight syringes equipped with an on/off valve were used to collect and store the pre-microwave treatment emissions for this study.

The gas-tight bags constructed of 2 mil Tedlar film are also used to collect air specimens. Tedlar is a polymeric material that is unaffected by most compounds and is impermeable to gas exchange. The bags are equipped with a septum for sample extraction using a syringe and an on/off valve to permit sample collection through a 6.0 mm I.D. Nalgene tube. A Tedlar bag was used to collect the gases emitted after microwave/thermal treatment. The results of the GCMS analyses on these two collection methods are shown in Table 5-10.

Table 5-10. GCMS Analysis of Emissions Prior To and After Microwave Treatment [Sch95].

Compound	Concentration (µg/device)	
	BEFORE (syringe)	AFTER (Tedlar bag)
1,3 Butadiyne	30.30	nd*
Chloromethane	18.73	nd
Bromo methane	36.89	nd
Ethyl benzene	6.25	nd
Styrene	5.71	nd
2-Butene, E	9.66	nd
1,3 Butadiene, 2-methyl	291	nd
1,2 Pentadiene	2.73	nd
Bromo ethane	3.93	nd
1-Pentene, 2-methyl	1.99	nd
1-Propene, 1-bromo	2.53	nd
1-Propene, 2-bromo	1.58	nd
Furan, tetrahydro	6.12	0.09
Furan, 2-methyl	33.94	nd
Butane, 1-bromo	18.49	nd
3-Octene, E	2.15	nd
p-Xylene (dimethyl benzene)	11.40	0.10
1,3,5 Trimethylbenzene (or)**	**1.69**	**0.09**
1,2,3 Trimethylbenzene (or)	**1.69**	**0.09**
1-Ethyl, 3-Methyl Benzene	**1.690**	**0.09**
1-Chloro-3-Methyl Benzene (or)*	***nd***	***0.13***
1-Chloro-2-Methyl Benzene	***nd***	***0.13***
Alpha-Methylstyrene	1.70	nd
Methylene Chloride	nd	0.07
Benzene (various other forms)	nd	0.04-0.11
Toluene	17.80	0.08

* = nd = not detected; ** computer could not differentiate between compounds

Tenax air traps

Borosilicate glass air traps filled with Tenax-TA, a polymeric material, are often used to collect air samples. Tenax-TA is a 2,6 diphenyl p-phenylene porous oxide polymer that is highly absorbent for C6-C20 compounds. Initial data collected over a 30 minute time period are summarized in Table 5-11. Tenax-TA traps were selected for future use for several reasons. First, the level of concentration of species found in initial data was thought to be more representative of actual emissions, and second, the trap was capable of collecting samples through the entire processing run, providing what was believed to be a more accurate sampling method when compared to periodic sampling for gas syringes and finally, ease of use when compared to the Tedlar bags. The Tenax-TA traps were used for all subsequent gas sampling experiments. Prior to use, the air traps were conditioned for one hour at 190°C as nitrogen flowed through the tube. This was done to remove organic binders and to dry the Tenax.

Repeatability Study

For this set of experiments, circuit boards from several circuit boards were obtained from discarded electronic equipment. Specifically, two CBs from a Sears Beta videocassette recorder (manufactured by Sanyo, 1983-84, VCR-4650) and five CBs reclaimed from a 1978 Regency scanner. The sample material was prepared as previously described by sectioning and crushing, and all boards were mixed together to simulate the random feed material that could be recovered from a landfill or scrap from an electronic manufacturing operation. Pyrolysis experiments were carried out in a 850W Goldstar Multiwave microwave that was connected (horizontal geometry)

Table 5-11. GCMS Data from Glass Air Trap Collection Method [Sch94].

Compound	Concentration (ng/tube) Before MW Treatment	Concentration (ng/tube) After MW Treatment
Benzene	3573000	nd
Chloromethane	3440000	nd
1,2,4-Trimethylbenzene	117000	37000
1,3-Dichlorobenzene	615000	nd
1,2-Dichlorobenzene	nd	42000
Chlorobenzene	nd	21000
Naphthalene	nd	3000
1,1-Dichlorethane	nd	3000

to the Amana 1000W microwave (Model RFS10B) that functioned as the off-gas unit. Each sample was processed for 30 minutes and emission specimens were collected throughout the processing regime. A summary of the GCMS data is presented in Table 5-12.

Similar experiments were carried out with the same feed material in the vertical microwave waste remediation system. These results are summarized in Table 5-13. As can be seen from the summary data in Tables 5-12 and 5-13, the concentration of gases was much higher for the vertical system than the horizontal system. This was believed to be due to improved air flow through the unit thus allowing more of the emissions to be passed through the interconnect and into the off-gas unit. Also, additional effort had been made to reduce the amount of emissions that escaped processing by leaking out of the combustion chamber by sealing seams, crevices and other avenues of possible escape. However, early data suggest that regardless of the geometry of the system, microwave energy was effective in reducing the concentration and number of aromatic compounds produced as a result of treating the waste circuitry.

Single Gas Experiments - Toluene Study

To try and better understand the influences of temperature and flow rate as well as the effects of microwave energy on the off-gases, a parametric study was initiated using a single compound found routinely in the emissions produced from destruction of the circuit boards. Toluene was selected for this study and was injected into the compressed air stream used to help evacuate the emissions from the combustion chamber. A set amount of toluene was injected into each run (1000μl). Temperature and flow rate, as well as heating method were altered. The results of the toluene study are summarized in Figure 5-5 and in Table 5-14 through Table 5-22 for samples treated with microwave energy and Table 5-23 through Table 5-27 for those samples

Table 5-12. A Summary of the GC Mass Spectroscopy Results of Emissions Resulting from Combustion of Printed Circuit Boards. (A = before microwave off-gas treatment; B = after microwave off-gas treatment).

Compound	SR-1 (ng/tube)		SR-2 (ng/tube)		SR-3 (ng/tube)		SR-4 (ng/tube)		SR-5 (ng/tube)		SR-6 (ng/tube)		SR-7 (ng/tube)	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Benzene*	16.9	1.1	14.2	<1	19.8	<1	115.3	5.2	119.6	8.1	176.6	14.7	165.4	13.5
Toluene*	28.7	2.7	24.4	<1	32.6	<1	67.5	6.1	78.7	6.9	159.1	18.1	115.7	5.9
Ethylbenzene*	18.7	<1	19.0	<1	7.8	<1	13.9	<1	26.7	<1	142.9	5.0	91.8	<1
Styrene*	38.7	1.2	66.6	<1	15.0	<1	165.2	2.9	167.7	2.6	472.3	27.2	482.9	6.5
Napthalene*	1.2	<1	11.0	<1	<1	<1	75.1	1.3	35.2	1.3	6.8	3.4	47.6	2.4
m/p Xylene*	17.5	<1	1.9	<1	<1	<1	27.5	<1	23.8	<1	53.3	1.6	60.0	<1
1,3,5 Trimethylbenzene	9.5	<1	12.4	<1	1.3	<1	15.6	1.6	18.4	<1	12.8	2.4	46.2	1.7
1,2,4 Trimethylbenzene	17.5	<1	1.7	<1	<1	<1	<1	<1	<1	<1	15.1	<1	6.1	1.8

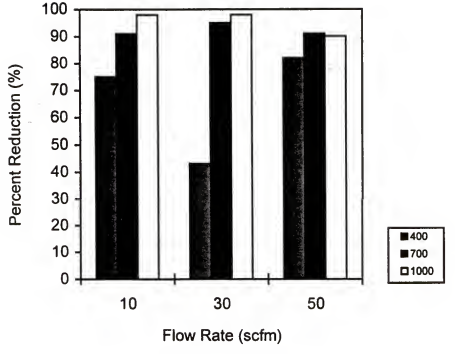
* Listed in the Clean Air Act (as amended, 1990) as hazardous air pollutants.

Table 5-13. Summary of Early GCMS Data from Vertical Off-Gas System.

Compound	SR-8 Emissions (ng/tube) A	SR-8 Emissions (ng/tube) B	SR-9 Emissions (ng/tube) A	SR-9 Emissions (ng/tube) B
Benzene	5838.9	22.2	1415.6	139.5
Toluene	8146.6	15.7	4215.9	158.7
Ethylbenzene	1147.4	nd*	4557.0	5.2
Styrene	1666.9	6.2	20012.0	38.4
Napthalene	355.5	nd	2403.6	27.9
m/p Xylene	2259.0	nd	510.6	nd
1,3,5 Trimethylbenzene	1564.0	nd	378.7	64.3
1,2,4 Trimethylbenzene	904.7	nd	171.8	nd

* not detected

A



B

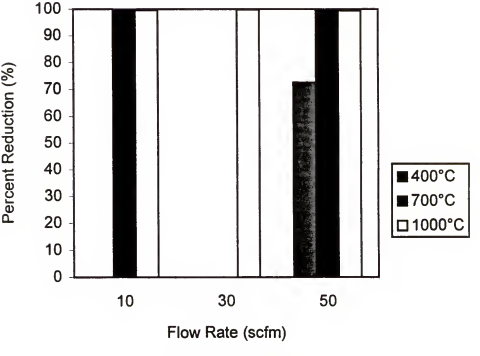


Figure 5-5. A) Percent reduction in concentration of toluene in single-gas study using microwave heating and; B) using conventional heating.

Table 5-14. The GCMS Data for the Toluene Study Conducted at 400°C, 10 ft^3/min, using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-400-10-1	400	10	50092.09	10697.34	78.64
PS-400-10-2	400	10	171645.17	47774.44	72.17

Table 5-15. The GCMS Data for the Toluene Study Conducted at 400°C, 30 ft^3/min, using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-400-30-1	400	30	46397.28	38621.94	16.76
PS-400-30-2	400	30	13801.04	4402.54	68.1

Table 5-16. The GCMS Data for the Toluene Study Conducted at 400°C, 50 ft^3/min, using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-400-50-1	400	50	26624.29	5818.65	78.15
PS-400-50-2	400	50	31670.23	4543.80	85.65

Table 5-17. The GCMS Data for the Toluene Study Conducted at 700°C, 10 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-700-10-1	700	10	12778.70	719.37	94.37
PS-700-10-2	700	10	19567.83	2411.29	87.68

Table 5-18. The GCMS Data for the Toluene Study Conducted at 700°C, 30 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-700-30-1	700	30	9992.87	1000.43	89.99
PS-700-30-2	700	30	169505.6	718.13	99.58

Table 5-19. The GCMS Data for the Toluene Study Conducted at 700°C, 50 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-700-50-1	700	50	7728.29	527.62	93.17
PS-700-50-2	700	50	12425.91	1288.13	89.63

Table 5-20. The GCMS Data for the Toluene Study Conducted at 1000°C, 10 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-1000-10-1	1000	10	7967.71	99.64	98.75
PS-1000-10-2	1000	10	20619.10	531.91	97.42

Table 5-21. The GCMS Data for the Toluene Study Conducted at 1000°C, 30 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-1000-30-1	1000	30	5561.59	111.82	97.99
PS-1000-30-2	1000	30	8710.29	194.73	97.76

Table 5-22. The GCMS Data for the Toluene Study Conducted at 1000°C, 50 ft^3/min using Microwave Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff. (%)
PS-1000-50-1	1000	50	7431.66	1239.98	83.31
PS-1000-50-2	1000	50	8261.85	256.28	96.90

Table 5-23. The GCMS Data for the Toluene Study Conducted at 400°C, 10 and 50 ft^3/min using Conventional Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff (%)
PSC-400-10-1	400	10			
PSC-400-50-1	400	50	7986.67	2185.38	72.64

Table 5-24. The GCMS Data for the Toluene Study Conducted at 700°C, 10 and 50 ft^3/min using Conventional Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff (%)
PSC-700-10-1	700	10	11742.80	81.78	99.30
PSC-700-50-1	700	50	9819.01	24.61	99.75

Table 5-25. The GCMS Data for the Toluene Study Conducted at 1000°C, 10ft³/min using Conventional Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff (%)
PSC-1000-10-1	1000	10	15266.93	22.54	99.85
PSC-1000-10-2	1000	10	11394.27	67.80	99.40

Table 5-26. The GCMS Data for the Toluene Study Conducted at 1000°C, 30 ft³/min using Conventional Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff (%)
PSC-1000-30-1	1000	30	15699.34	1.38	99.99
PSC-1000-30-2	1000	30	5944.75	26.11	99.56

Table 5-27. The GCMS Data for the Toluene Study Conducted at 1000°C, 50 ft³/min using Conventional Heating.

SAMPLE ID	OFF-GAS TEMP (°C)	FLOW RATE (ft^3/min)	GCMS Results (ng/tube) A	B	Percent Diff (%)
PSC-1000-50-1	1000	50	1053.86	13.19	98.75
PSC-1000-50-2	1000	50	1425.43	26.02	98.17

treated with conventional heating. As can be seen from the data, there is little difference in the performance of the microwave system when compared to the conventionally heated system. It did appear that both systems performed somewhat better at higher temperatures (700-1000°C). This is to be expected as the autoignition temperature for toluene is 553°C [Bru96]. Autoignition temperature is defined as the temperature where the gas will combust. To sustain combustion, an excess of air is required and the concentration of gas to be combusted must be maintained between the lower and upper explosion limit (1.3-7.0 % by volume for toluene) [Bru96]. The decomposition reaction is as follows:

$$C_7H_8 + 9O_2 \xrightarrow[553°C]{} 7CO_2 + 4H_2O \qquad 5\text{-}1$$

Since this exact ratio was most likely not attained with the current system, it is reasonable to assume that other combustion by-products were present (for example, CO) and complete destruction of toluene was not attained. This supposition is supported by the data in cases where the percent reduction was less than 100%. The data also show that for the flow rates selected, there was no real discernable difference with changes in flow rate.

There also did not appear to be a real difference between heating methods. There are several possible reasons for this. The first, is that microwave energy, at this frequency, has no effect on the gaseous species. A second possibility may be that the SiC used to attain the temperatures necessary to decompose the gases is absorbing most or all of the microwave energy and the only heating taking place within the off-gas chamber is through radiant heating. As mentioned earlier, SiC is highly susceptible to microwave radiation. Using equation 4.8, and data acquired from Batt et al. [Bat95], the depth of penetration for SiC can be calculated and gives a

value of 0.135cm at 2.45GHz at room temperature. Depth of penetration would increase with increases in temperature as it is a function of tanδ. On first inspection it may seem that this penetration depth is too small to result in volumetric heating of the SiC filters which have a diameter of approximately 5cm. However, a description of the SiC filters which consist of a porous structure (25pore/in) connected by thin sections with diameters less than the penetration depth provides a possible explanation for volumetric heating within the filters, as each small connecting section can be heated volumetrically, resulting in volumetric heating of the whole filter. If most or all of the microwave energy is absorbed by the SiC, little or no microwave energy is available for absorption by the gaseous products passing through the system.

For the systems tested in this study, residence time is a factor of flow rate. For the microwave off-gas system shown in Figure 5-6, the refractory cylinder was packed with 7 SiC reticulated ceramic filters and 2 phosphate-bonded alumina filters (1 at each end of the cylinder). Each filter had a volume of approximately 1.9×10^{-4} ft^3 and there were a total of 9 filters. The cylinder had a volume of 1.62×10^{-2} ft^3. Residence time as a function of flow rate is as follows:

$$t_R = \frac{vol.\ of\ cylinder\ (ft^3) - vol.\ of\ filters\ (ft^3)}{flow\ rate\ (ft^3/\min)} \qquad 5.2$$

With a calculated volume for the refractory cylinder less the volume of the filters equal to approximately 1.45×10^{-2} ft^3, a summary of the calculated results is as follows:

Flow Rate (ft^3/min)	Residence Time (sec)
10	8.7×10^{-2}
30	2.9×10^{-2}
50	1.7×10^{-2}

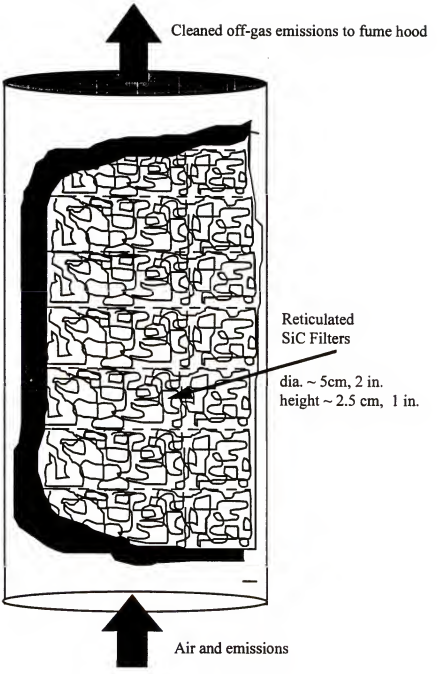


Figure 5-6. Schematic illustration of microwave susceptor off-gas bed (SiC reticulated ceramic filters).

Also, for both systems described, the off-gas chamber was already at temperature (a fuel/waste gas mixture was not ignited and burned to gain the desired temperature) when the emissions entered the chamber. Therefore, for the microwave system (or the conventional system used here) it would be relatively simple to increase the dwell time for a gaseous species by simply increasing the heated area of the cavity or adjusting the flow rate. It should be noted that the flow rate for these systems serves two purposes. While one purpose is to help maintain an adequate residence time, the other is to ensure that the combustion chamber is not flooded with emissions. If the emissions are not moved out of the combustion chamber at a sufficient rate, they tend to find other avenues of escape, such as door crevices or though other openings designed by the manufacturer. These emissions are released to the hood area without treatment.

In conventional incineration techniques, residence or dwell time is defined as the amount of time required for initiation and completion of the oxidation process and is a function of temperature, turbulence and fuel particle size [Bru96, Pat94]. However, it may be more accurate to refer to this as a reaction time. The equation that describes reaction (residence) time is as follows [Nie95]:

$$t = \frac{C_{p,av}\Delta T}{q_v} \qquad 5.3$$

where:

t = residence time (sec)

$C_{p,av}$ = gas heat capacity (kcal $m^{-3}°C^{-1}$) over range of ΔT

ΔT = required temperature rise (°C)

q_v = combustion intensity (kcal sec^{-1} m^{-3})

In practice it is often assumed that residence time is a constant because it is believed that the process steps are fixed [Nie95].

Another method often used to calculate reaction rates and time in practice is as follows [DeN95]:

$$\frac{-dC_A}{dt} = r = kc_A^n \qquad 5.4$$

where:

$-dC_A/dt$	=	decrease in concentration of species A per unit time
r	=	reaction rate
k	=	a kinetic rate constant, strongly dependent on temperature, but not concentration
c_A	=	concentration of species A
n	=	reaction order

By integrating equation 5.4 from t = 0 to t = t, assuming a first order reaction(n = 1), inserting known values for k (at 760°C), c_A (0.001 for a 99.9 removal efficiency) a reaction time equal to approximately 0.2 seconds is calculated for benzene. Similar calculations carried out for a temperature of 538°C yields a reaction time of 17.4 hours. Therefore, the dependence on temperature is clearly seen. It should also be noted that the microwave system was able to reduce the concentration of benzene by 99.9% at 400°C and a flow rate of 10 scfm. This corresponds to an estimated residence time of 0.087 seconds. Similar results were obtained for flowrates of 30 and 50 scfm, corresponding to even shorter residence times. Similar results were also

obtained with the conventional off-gas system tested. It is speculated that the SiC bed may have acted as a catalyst and helped reduce reaction (residence) times.

As can be seen in the GCMS data tables, a percent difference column was included. This value was calculated using the following formula:

$$\% \; diff = \frac{X_i - X_f}{X_i} \; x \; 100 \qquad 5.5$$

where:

X_i = concentration of gas prior to treatment

X_f = concentration of gas after treatment

This is a close approximation to the destruction and removal efficiency (DRE) equation used to calculate the effectiveness of treatment processes in commercial and industrial waste incinerators. The DRE equation is as follows [Bru96]:

$$DRE = \frac{W_i - W_o}{W_i} \; x \; 100 \qquad 5.6$$

where:

W_i = mass of the principle organic hazardous component (POHC) into the system

W_o = mass of the POHC leaving the system in the incinerator exhaust.

For most hazardous wastes, a DRE of at least 99.99% is required in order for the incineration process to be considered effective. For some species, a DRE of 99.9999% is required (dioxin, polychlorinated biphenyls, furans). Since the mass of the aromatic hydrocarbons entering and

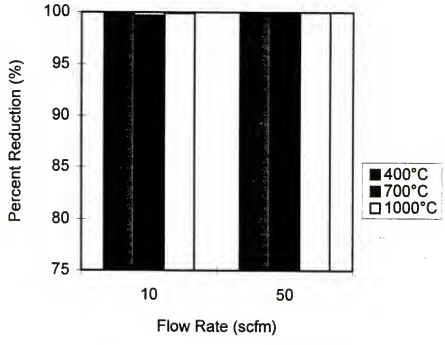
leaving the off-gas is unknown, a calculation of the percent difference in concentration of the species detected in the air trap by GCMS provides only an approximation of the efficiency of the microwave and conventional systems tested during this study.

Pantex Defense Electronic Circuitry

The gas chromatography-mass spectroscopy data collected for the microwave portion of the study is summarized in Figures 5-7 through 5-9 which show the percent reduction in benzene, toluene and styrene as a function of temperature, flow rate and heating method. The complete GCMS data is summarized in Table 5-28 through Table 5-36 for gas samples heated using microwave energy. Similar data collected for gas samples heated using conventional methods are shown in Tables 5-37 through Table 5-43.

The GCMS data generated from the Pantex circuit board study is consistent with the single gas toluene data in that there was no clear distinction between microwave and conventional heating, regardless of the organic compound, temperature or flowrate. The only species where one may make a case for a difference between heating methods is styrene, where it appears that microwave energy may be slightly more efficient in decomposing this compound. However, further testing is necessary to be sure the results consistently repeat this trend. This data also tends to support the molecular orbital/coupled oscillator model in that for benzene and toluene in that the microwave absorption peaks were not centered at 2.45GHz, but were located at other microwave frequencies. There was a very weak absorption peak for benzene located at approximately 2.3 GHz where a slight interaction with microwave energy at the applied frequency may have occurred, but because a stronger absorption peak was located at ~8.3GHz,

A



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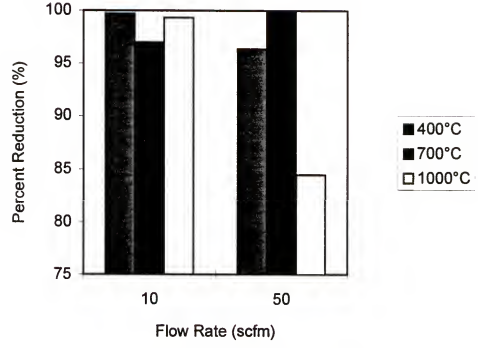
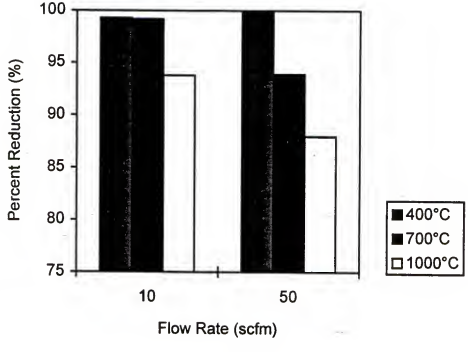
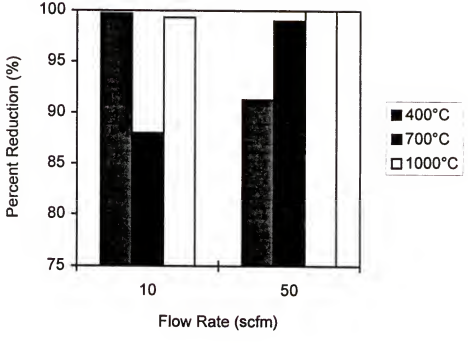


Figure 5-7. A) Percent reduction in concentration of benzene from circuit board destruction using microwave heating and; B) using conventional heating.



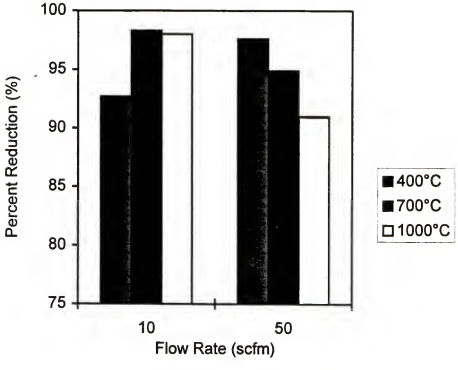
A



B

Figure 5-8. A) Percent reduction in concentration of toluene from circuit board destruction using microwave heating and; B) using conventional heating.

A



B

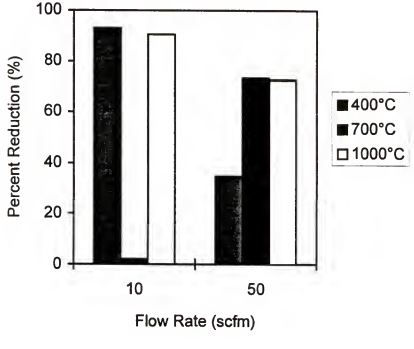


Figure 5-9. A) Percent reduction in concentration of styrene from circuit board destruction using microwave heating and; B) using conventional heating.

Table 5-28. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards (400°C, 10scfm).

Compound	MW1-400-10 (ng/tube) PRE	POST	% Diff.	MW2-400-10 (ng/tube) PRE	POST	% Diff.
Benzene	5609.20	5.34	99.90	10135.23	39.84	99.61
Toluene	1101.71	10.15	99.08	3205.38	15.88	99.50
m-Xylene	154.94	nd	100	427.31	nd	100
p-Xylene	52.08	1.77	96.60	139.31	2.63	98.11
Ethynylbenzene	271.56	7.69	97.17	721.86	1.02	99.86
Styrene	195.28	28.20	85.56	2445.21	6.03	99.75
Bromobenzene	34.69	nd	100	90.78	nd	100
Ethymethylbenzene	1.14	nd	100	5.36	nd	100
1,3,5 Trimethylbenzene	nd	nd	--	5.14	nd	100
1,2,4 Trimethylbenzene	1.14	nd	100	2.67	nd	100
Isopropylbenzene	nd	nd	--	10.66	nd	100

Table 5-29. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards (400°C, 30scfm).

Compound	MW1-400-30 (ng/tube) PRE	POST	% Diff.	MW2-400-30 (ng/tube) PRE	POST	% Diff.
Benzene	4167.88	427.14	89.75	7294.41	4.28	99.94
Toluene	708.39	33.46	95.28	841.15	5.56	99.34
m-Xylene	43.86	3.28	92.52	9.66	nd	100
p-Xylene	67.33	9.24	86.28	134.66	nd	100
Ethynylbenzene	13.64	3.20	76.54	710.56	nd	100
Styrene	62.06	16.32	73.70	593.86	2.76	99.54
Bromobenzene	22.88	30.83	+25.79	40.01	nd	100
Ethymethylbenzene	4.04	nd	100	nd	nd	--
1,3,5 Trimethylbenzene	3.92	nd	100	1.95	nd	100
1,2,4 Trimethylbenzene	nd	nd	--	nd	nd	--
Isopropylbenzene	9.20	nd	100	nd	nd	--

Table 5-30. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards (400°C, 50scfm).

Compound	MW1-400-50 (ng/tube) PRE	POST	% Diff.	MW2-400-50 (ng/tube) PRE	POST	% Diff.
Benzene	3980.34	1.14	99.97	2256.90	nd	100
Toluene	6667.96	2.64	99.96	401.71	nd	100
m-Xylene	35.15	nd	100	10.17	nd	100
p-Xylene	96.27	nd	100	104.34	nd	100
Ethynylbenzene	65.65	1.29	98.03	171.35	nd	100
Styrene	119.69	4.17	96.52	118.17	1.65	98.60
Bromobenzene	27.47	nd	100	20.40	nd	100
Ethymethylbenzene	4.50	nd	100	5.28	nd	100
1,3,5 Trimethylbenzene	3.63	nd	100	4.42	nd	100
1,2,4 Trimethylbenzene	4.49	nd	100	5.26	nd	100
Isopropylbenzene	nd	nd	--	1.22	nd	100

Table 5-31. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (700°C, 10scfm).

Compound	MW1-700-10 (ng/tube) PRE	POST	% Diff.	MW2-700-10 (ng/tube) PRE	POST	% Diff.
Benzene	4307.39	7.74	99.82	1808.53	8.84	99.51
Toluene	1139.17	16.23	98.57	651.15	1.74	99.73
m-Xylene	61.52	nd	100	65.45	nd	100
p-Xylene	65.29	nd	100	79.07	nd	100
Ethynylbenzene	385.30	nd	100	21.95	nd	100
Styrene	868.70	nd	100	66.90	2.22	96.68
Bromobenzene	58.66	nd	100	22.81	nd	100
Ethymethylbenzene	nd	nd	--	4.42	nd	100
1,3,5 Trimethylbenzene	1.37	nd	100	5.92	nd	100
1,2,4 Trimethylbenzene	nd	nd	--	2.39	nd	100
Isopropylbenzene	nd	nd	--	6.22	nd	100

Table 5-32. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (700°C, 30scfm).

Compound	MW1-700-30 (ng/tube) PRE	POST	% Diff.	MW2-700-30 (ng/tube) PRE	POST	% Diff.
Benzene	2318.43	nd	100	5138.69	1.52	99.97
Toluene	300.43	20.70	93.11	957.11	8.79	99.08
m-Xylene	6.46	1.00	84.52	28.86	nd	100
p-Xylene	32.72	1.01	96.91	62.85	nd	100
Ethynylbenzene	87.54	nd	100	131.22	nd	100
Styrene	44.46	1.96	95.59	114.65	1.16	98.91
Bromobenzene	27.16	nd	100	43.15	nd	100
Ethymethylbenzene	2.47	nd	100	3.32	nd	100
1,3,5 Trimethylbenzene	2.34	nd	100	4.35	nd	100
1,2,4 Trimethylbenzene	2.46	nd	100	1.40	nd	100
Isopropylbenzene	1.23	nd	100	3.60	nd	100

Table 5-33. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (700°C, 50scfm; NA = data unavailable).

Compound	MW1-700-50 (ng/tube) PRE	POST	% Diff.	MW2-700-50 (ng/tube) PRE	POST	% Diff.
Benzene	533.22	nd	100	NA	48.29	--
Toluene	198.46	11.98	93.96	NA	8.61	--
m-Xylene	29.78	nd	100	NA	nd	--
p-Xylene	40.49	3.79	90.64	NA	nd	--
Ethynylbenzene	6.10	nd	100	NA	nd	--
Styrene	34.44	1.74	94.95	NA	nd	--
Bromobenzene	7.51	nd	100	NA	4.89	--
Ethymethylbenzene	1.56	nd	100	NA	nd	--
1,3,5 Trimethylbenzene	2.48	nd	100	NA	nd	--
1,2,4 Trimethylbenzene	1.33	nd	100	NA	nd	--
Isopropylbenzene	1.82	nd	100	NA	nd	--

Table 5-34. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (1000°C, 10scfm).

Compound	MW1-1000-10 (ng/tube) PRE	POST	% Diff.	MW2-1000-10 (ng/tube) PRE	POST	% Diff.
Benzene	2932.00	1.03	99.96	4422.97	2.28	99.95
Toluene	785.37	61.99	92.1	777.87	35.84	95.39
m-Xylene	36.00	nd	100	66.46	nd	100
p-Xylene	127.00	nd	100	131.08	nd	100
Ethynylbenzene	28.00	nd	100	80.11	nd	100
Styrene	141.00	4.43	96.86	184.56	1.56	99.15
Bromobenzene	30.00	nd	100	26.24	nd	100
Ethymethylbenzene	14.00	nd	100	9.01	nd	100
1,3,5 Trimethylbenzene	16.00	nd	100	18.87	nd	100
1,2,4 Trimethylbenzene	5.90	nd	100	6.73	nd	100
Isopropylbenzene	5.90	nd	100	10.80	nd	100

Table 5-35. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (1000°C, 30scfm).

Compound	MW1-1000-30 (ng/tube) PRE	POST	% Diff.	MW2-1000-30 (ng/tube) PRE	POST	% Diff.
Benzene	2799.86	2.98	99.89	1142.56	1.46	99.87
Toluene	863.80	239.97	72.22	623.05	44.26	92.89
m-Xylene	219.78	1.43	99.34	76.72	nd	100
p-Xylene	95.70	3.39	96.45	145.85	nd	100
Ethynylbenzene	41.09	nd	100	12.83	nd	100
Styrene	1361.31	nd	100	333.61	2.03	99.39
Bromobenzene	19.41	nd	100	13.66	nd	100
Ethymethylbenzene	7.06	nd	100	7.37	nd	100
1,3,5 Trimethylbenzene	9.84	nd	100	8.37	nd	100
1,2,4 Trimethylbenzene	4.59	nd	100	4.26	nd	100
Isopropylbenzene	6.06	nd	100	4.34	nd	100

Table 5-36. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Microwave Heating (1000°C, 50scfm).

Compound	MW1-1000-50(ng/tube) PRE	POST	% Diff.	MW2-1000-50 (ng/tube) PRE	POST	% Diff.
Benzene	1307.81	nd	100	1145.08	1.14	99.90
Toluene	367.50	45.33	87.66	321.09	35.90	88.82
m-Xylene	24.95	nd	100	29.44	nd	100
p-Xylene	60.43	nd	100	87.11	1.80	97.93
Ethynylbenzene	50.56	nd	100	21.28	nd	100
Styrene	61.56	10.57	82.83	88.12	1.57	99.16
Bromobenzene	20.49	nd	100	11.39	nd	100
Ethymethylbenzene	4.23	nd	100	3.16	nd	100
1,3,5 Trimethylbenzene	4.72	nd	100	5.01	nd	100
1,2,4 Trimethylbenzene	2.50	nd	100	1.59	nd	100
Isopropylbenzene	3.22	nd	100	1.94	nd	100

Table 5-37. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (400°C, 10scfm).

Compound	CON1-400-10 (ng/tube) PRE	POST	% Diff.
Benzene	966.25	3.34	99.65
Toluene	412.89	1.12	99.73
m-Xylene	1025.47	nd	100
p-Xylene	32.38	nd	100
Ethynylbenzene	63.33	1.57	97.52
Styrene	196.79	13.90	92.94
Bromobenzene	4.55	1.41	69.01
Ethymethylbenzene	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--
1,2,4 Trimethylbenzene	nd	nd	--
Isopropylbenzene	nd	nd	--

Table 5-38. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (400°C, 50scfm).

Compound	CON1-400-50 (ng/tube) PRE	POST	% Diff.
Benzene	196.57	7.06	96.41
Toluene	131.00	11.40	91.29
m-Xylene	20.22	1.39	93.13
p-Xylene	20.34	1.39	93.17
Ethynylbenzene	1.44	nd	100
Styrene	24.37	15.90	34.75
Bromobenzene	5.89	1.42	75.89
Ethymethylbenzene	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--
1,2,4 Trimethylbenzene	nd	nd	--
Isopropylbenzene	nd	nd	--

Table 5-39. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (700°C, 10scfm).

Compound	CON1-700-10 (ng/tube) PRE	POST	% Diff.
Benzene	360.62	10.74	97.02
Toluene	180.29	21.21	88.24
m-Xylene	11.76	2.84	75.85
p-Xylene	58.05	2.85	95.09
Ethynylbenzene	2.85	10.06	+71.67
Styrene	21.59	21.15	2.04
Bromobenzene	7.92	1.12	85.86
Ethymethylbenzene	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--
1,2,4 Trimethylbenzene	nd	nd	--
Isopropylbenzene	nd	nd	--

Table 5-40. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (700°C, 50scfm).

Compound	CON1-700-50 (ng/tube) PRE	POST	% Diff.
Benzene	536.78	nd	100
Toluene	177.93	1.57	99.12
m-Xylene	2.11	1.45	31.28
p-Xylene	29.97	1.83	93.89
Ethynylbenzene	3.81	nd	100
Styrene	11.10	2.96	73.33
Bromobenzene	3.90	1.96	49.74
Ethymethylbenzene	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--
1,2,4 Trimethylbenzene	nd	nd	--
Isopropylbenzene	nd	nd	--

Table 5-41. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (1000°C, 10scfm).

Compound	CON1-1000-10 (ng/tube) PRE	POST	% Diff.	CON2-1000-10 (ng/tube) PRE	POST	% Diff.
Benzene	664.42	9.61	98.55	18641.03	nd	100
Toluene	3275.48	12.35	99.62	1735.08	18.11	98.96
m-Xylene	30.82	nd	100	98.94	nd	100
p-Xylene	52.57	nd	100	99.50	13.28	86.65
Ethynylbenzene	nd	nd	---	5.43	nd	100
Styrene	49.53	nd	100	252.56	47.41	81.23
Bromobenzene	5.85	5.44	7.00	28.02	15.27	45.50
Ethymethylbenzene	nd	nd	--	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--	nd	nd	--
1,2,4 Trimethylbenzene	nd	nd	--	nd	nd	--
Isopropylbenzene	nd	nd	--	nd	nd	--

Table 5-42. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (1000°C, 30scfm).

Compound	CON1-1000-30 (ng/tube) PRE	POST	% Diff.	CON2-1000-30 (ng/tube) PRE	POST	% Diff.
Benzene	NA	4.01	--	676.74	nd	100
Toluene	NA	28.89	--	241.00	nd	100
m-Xylene	NA	nd	--	12.07	nd	100
p-Xylene	NA	nd	--	40.97	nd	100
Ethynylbenzene	NA	nd	--	147.18	nd	100
Styrene	NA	nd	--	81.28	60.84	25.15
Bromobenzene	NA	1.52	--	22.31	nd	100
Ethymethylbenzene	NA	nd	--	nd	nd	--
1,3,5 Trimethylbenzene	NA	nd	--	nd	nd	--
1,2,4 Trimethylbenzene	NA	nd	--	nd	nd	--
Isopropylbenzene	NA	nd	--	nd	nd	--

Table 5-43. The GCMS Data Compiled for Emissions Generated from Pantex Circuit Boards using Conventional Heating (1000°C, 50scfm).

Compound	CON1-1000-50 (ng/tube) PRE	POST	% Diff.	CON2-1000-50 (ng/tube) PRE	POST	% Diff.
Benzene	62.78	15.78	74.86	360.46	20.92	94.19
Toluene	219.26	nd	100	109.85	nd	100
m-Xylene	98.03	nd	100	7.09	nd	100
p-Xylene	48.52	nd	100	10.89	nd	100
Ethynylbenzene	59.22	nd	100	4.42	nd	100
Styrene	2198.21	nd	100	31.55	17.35	45.00
Bromobenzene	18.62	94.44	+80.28	4.37	nd	100
Ethymethylbenzene	nd	nd	--	nd	nd	--
1,3,5 Trimethylbenzene	nd	nd	--	nd	nd	--
1,2,4 Trimethylbenzene	nd	233.08	+100	nd	nd	--
Isopropylbenzene	1.40	nd	100	nd	nd	--

a strong interaction would not be predicted at 2.45GHz. The absorption peaks for toluene were in the 25-70 GHz range, so one may not expect this gas to decompose solely due to exposure to microwave energy. The exception is styrene, which according to the modeling data, is expected to absorb microwave energy at a frequency of ~3.6 GHz. However, the peak is distributed over a wide range of frequency and it is possible that coupling is occurring not at the peak maxima, but at the applied frequency which lies on the left side of the curve. Further testing is required to verify these findings.

In some cases, gas compounds were found in the air stream that were either, not present, or found in smaller concentrations in the pre-treated sample (bromobenzene and 1,2,4 trimethylbenzene). One proposed explanation may be that these compounds represent intermediate breakdown products of other species in the waste gas and that the temperatures or residence times in the off gas system were insufficient to destroy them prior to release. However, if this were the case, one would expect this trend to be found consistently throughout the study. This was not the case. Therefore, this phenomenon remains unexplained and warrants further study.

Overall, the results of this study reveal that both systems appear to function well and are reasonably efficient in destroying a mixed waste gas air stream consisting primarily of aromatic hydrocarbons. As these compounds represent a threat to the health of the population given sufficient exposure and concentration, the value of the microwave waste gas system is clear. However, to develop the system to its full potential requires additional study.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The recyclability of electronic circuitry using microwave energy has been shown to be possible as a result of this study. Polymeric portions of electronic components have been decomposed using microwave radiation. The resulting gaseous products were then processed in an effort to decompose or destroy them prior to release to the environment. The remaining components, glass reinforcements, ceramics and metals were heated to temperatures sufficient to cause vitrification and melting of the metals. It is believed that the glass product can be utilized for a variety of purposes such as construction products, or possibly be used to create new fiber reinforcements for new circuit boards. The recovered metals can be refined through conventional practices, or possibly in the future, via selective microwave heating methods and made available for resale.

In addition to defining a method for the remediation of waste circuitry using microwave energy, laboratory-scale equipment has been developed and refined to treat circuitry waste. Though not elaborated upon in this dissertation, the equipment has also been used to test the efficacy of microwave energy on other waste materials including: transuranic wastes, simulated medical waste, used rubber materials and liquid chemical wastes.

The objectives of this study, as outlined in the Introduction section were first, to develop a microwave waste treatment system that would allow treatment of all circuitry presented for destruction and recovery operations. This has been accomplished, however further refinements (as described in the following chapter) could improve the overall performance of the system. The second objective was to develop a methodology using microwave energy to vitrify the ash and recover metallic components. Using the Raytheon microwave, it was possible to vitrify the ash without adding any additional glass formers and to recover the metal components. It appears that most of the precious metals are contained in the metal ingot and are not bound in the glass. Furthermore, analyses indicate that at least a portion of the hazardous materials found in the circuit board were encapsulated in the glass (e.g., Be, Cd, As). It has yet to be determined if any of the heavy metals were present in the off gas waste stream. The third objective was to develop a microwave off-gas system capable of destroying or decomposing the emissions that result from processing the circuitry waste. A series of experiments were carried out to determine the effects of temperature and residence time on the emissions. Gas chromatography/mass spectroscopy results on emissions from the circuitry as well as on the single gas toluene study indicate that the microwave is effective in reducing the concentration of the emissions. In most cases higher temperatures were more effective than the lower temperatures tested, and the flow rates selected did not seem to have much effect on the destruction of the species. The fourth objective was to determine the mechanisms and extent of microwave radiation on the waste circuitry and the products of interaction (solids and gases). Microwave energy was shown to be effective in removing the organics from the circuitry. With continued application of

microwave energy at higher power levels, vitrification and metal recovery was possible. With respect to the interaction of the microwave energy with the gaseous products, when compared to heating with conventional methods, the results show that the microwave is at least as efficient, and in some cases (styrene) perhaps more effective than conventional heating. Further testing is required to verify whether or not this is actually the case. Finally, modeling the behavior of some of the gases generated during processing of circuitry was carried out through the use of computer modeling techniques based on molecular orbital/coupled oscillator theory. The model suggests that microwaves are absorbed directly by the resonance frequency of coupled oscillators. Preliminary data indicates that the model correlates fairly well with experimental results.

Other data or observations that resulted from the various experiments carried out during the study are summarized in the following paragraphs.

➢ A variety of different types of electronic circuitry can be processed using microwave energy. These include components from computers, entertainment and communication equipment, defense-related circuitry (trajectory switches, firesets, and Pantex feed), and commercial transistors. In most cases, processing resulted in a significant volume and weight reduction when compared to the starting material. These reductions would have a substantial impact on the amount of waste to be landfilled if the material were not recycled by additional processing.

➢ By continuing with the proposed processing scheme, the circuitry was further reduced in volume and two products with a potential commercial value were produced. These were a glass product and metal ingots. The value of the glass as an additive in

construction or as a feed material in another process has yet to be determined. Based on the current price of gold (292.50/oz as of 09/21/98), the value of the recovered gold is estimated at $1950 per ton of circuitry processed. The value of the other metals would be determined by current market values and the ease with which they could be extracted from the amalgamated metal ingot.

➢ Through an experimental evolutionary process, a laboratory-scale microwave waste processing system was designed and fabricated. The system, in its final form, consisted of two 900W microwaves connected in tandem in a vertical configuration. The lower chamber was used to remove the organics from the electronic components. The upper chamber contained a refractory cylindrical housing filled with SiC filters and particulates. The system was capable of pyrolyzing various wasteforms while simultaneously subjecting numerous volatile and aromatic gaseous hydrocarbons to both high temperatures and microwave radiation. Gas chromatography/mass spectroscopy analyses of the gases revealed a measurable decrease in the concentration of the various gases as well as a decrease in the number of compounds available for release to the atmosphere. This would appear to indicate a partial decomposition in some cases, and in others, a complete breakdown of the gases as they pass through the microwave off-gas chamber.

➢Through the work of other researchers and the results obtained from this study, it has been demonstrated that microwave energy is a valuable tool for use in the waste remediation area. Some of the reasons that exemplify the unique capabilities of microwave energy are its flexibility both in equipment design and processing capabilities, it can be made

remote eliminating or reducing the risk of exposure to personnel and equipment, selective and rapid heating are possible, as are potential energy savings.

➢ Results from the computer modeling indicate microwave frequencies where some of the gases found in the wastestream should interact. The physical mechanism believed to be responsible for microwave absorption is coupled molecular vibrations. The source of the coupled oscillators in ceramic materials is thought to be defects on a particle surface or in the grain boundary. For the gases it is believed to be dangling bonds.

Conclusions

The following conclusions can be drawn from this study:

➢ It is possible to completely destroy an electronic component using microwave energy. In the process, two recyclable materials are produced and recovered - glassy product and metal ingot(s).

➢The microwave off-gas system is capable of destroying or decomposing a range of hazardous gaseous products (e.g., benzene, toluene, styrene, naphthalene, xylene).

➢The microwave off-gas system is at least as effective in destroying emissions as the conventional system. The microwave system may offer some advantages in that electronics and other expendable components (magnetron) can be made remote, design capabilities are flexible, and in some cases it may be more cost efficient.

CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

The following are some recommendations that would be beneficial in advancing the work carried out in this study:

➢ With respect to equipment development, computer control of temperature, flow rate and duty cycles should be implemented. This would increase efficiency of processing and aid in scale-up operations.

➢ It was speculated that the SiC in the off-gas system was absorbing most of the microwave energy leaving little or no energy free to interact with the gaseous species. Altering the off-gas bed material to a substance that does not interact with microawaves as efficiently as SiC would aid in determination of the effect of microwave energy on the gaseous species. Also, tailoring the bed to be adsorption specific for certain types of waste that could trap species and prevent their release to the atmosphere while allowing additional residence time within the chamber, continued exposure to microwave energy and perhaps their eventual destruction.

➢ Additional tests on other pure single gases and mixed (2 or more pure gases) should be tested.

➢More complete characterization of the off-gases must be carried out to determine the true effectiveness of microwave treatment. It has yet to be ascertained whether or not the

system has any effect on dioxins, polychlorinated biphenyls, heavy metals, NO_x, acidity levels, or other potentially harmful gaseous air pollutants. If the microwave off-gas system is ineffective in treating certain air pollutants, other bed materials should be determined and tested, along with finding additional methods (increasing temperature, residence time, and altering the applied frequency) that would insure complete destruction of all hazardous gases.

➢ Refine the gas collection method or adopt one of the standardized EPA air collection methods (VOST or Semi-VOST).

➢Continue to test other waste materials in the system (infectious/biological wastes, foodstuffs, chemical wastes, volume reduction of household wastes, others).

➢ Scale-up to pilot plant level would provide a true test of the economic and practical viability of the technology.

➢ Experimental verification of current coupled oscillator models is necessary in order to determine the validity and accuracy of the proposed model. Also, continued work in the area of computer modeling toward a better understanding of the mechanisms responsible for microwave/material interactions.

APPENDIX

Modeling Studies

There has been much discussion in the literature about how microwaves couple with materials. Also, there have been reports of a microwave "effect" by several researchers. These effects include enhanced reaction rates, different reaction pathways and improved properties. For example, the primary mechanism of microwave absorption by most polymers is thought to be through the oscillation of a dipole moment caused by the applied electric field [Lew93, Che93a, Che93b, Che93c, Che95, Wei93]. The dipole moment is formed by adjacent groups with differing electron charges. Typical groups which form dipoles are hydroxy, amino and cyanate groups. When no electric field is present, the charges are randomly oriented throughout the material. However, when an electric field is applied, the dipoles tend to orient themselves with the field. The extent to which the dipole moments can be oriented depends on the mobility and strength of the dipole moment and the electric field. When a low frequency alternating field is applied the dipole moments oscillate in phase with the field, storing the energy of the alternating electric field. As the frequency increases, the dipoles can no longer keep up with the changing direction of the field resulting in losses of the stored energy from the field or to absorption of energy by the material [Lew93]. This energy is converted to heat.

Although the mechanisms discussed in the above sections (i.e., dipolar and conduction losses) may be responsible for interactions in some materials, none of these mechanisms should be operative at microwave frequencies. Thus, the purpose of this section is to discuss a new mechanism and models still under development for both microwave material/interactions and the microwave "effect." First, a proposed model developed by John West at the University of Florida using quantum molecular orbital theory (MO) together with coupled oscillator theory is discussed to explain how materials with no obvious coupling mechanisms in the microwave frequency range can in fact, couple with certain microwave frequencies. This work is currently under development. All figures and data tables shown in this appendix are attributed to his as yet unpublished work.

The model proposed by West for is applicable for microwave interactions with solids, liquids and gases. In addition, preliminary data has been generated for some of the emissions evolved during the combustion of the electronic circuitry. In this study, it was suggested that coupled oscillators formed from two nearby defect structures, or structures with dangling bonds (as in the case of gases) that may have frequencies that are close to, or can be shifted to frequencies in the microwave region. In the MO study, structures that should have had identical vibrations, but did not, were targeted for investigation. The difference between the two calculated vibrations is associated with the secondary frequency of a coupled oscillator. These secondary oscillator sites are prospective areas where microwave coupling (absorption) could occur (see Figure A-1).

The mathematics behind quantum molecular orbital theory, coupled oscillators, as well as the parameters for the Austin-Method1 (AM1) program are provided in the literature

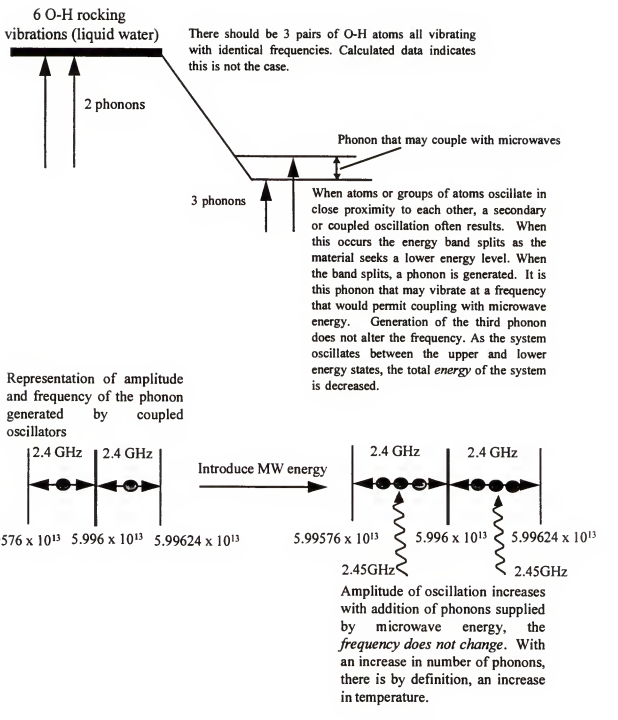

6 O-H rocking vibrations (liquid water)
There should be 3 pairs of O-H atoms all vibrating with identical frequencies. Calculated data indicates this is not the case.
2 phonons
Phonon that may couple with microwaves
3 phonons
When atoms or groups of atoms oscillate in close proximity to each other, a secondary or coupled oscillation often results. When this occurs the energy band splits as the material seeks a lower energy level. When the band splits, a phonon is generated. It is this phonon that may vibrate at a frequency that would permit coupling with microwave energy. Generation of the third phonon does not alter the frequency. As the system oscillates between the upper and lower energy states, the total energy of the system is decreased.
Representation of amplitude and frequency of the phonon generated by coupled oscillators
2.4 GHz
2.4 GHz
Introduce MW energy
2.4 GHz
2.4 GHz
5.99576 x 10^13
5.996 x 10^13
5.99624 x 10^13
5.99576 x 10^13
5.996 x 10^13
5.99624 x 10^13
2.45GHz
2.45GHz
Amplitude of oscillation increases with addition of phonons supplied by microwave energy, the frequency does not change. With an increase in number of phonons, there is by definition, an increase in temperature.

Figure A-1. Representation of the formation of coupled oscillators and the effect of microwave energy.

[Wes94, Wes95]. The interested reader is referred to the literature for a more detailed explanation of the calculations involved in determining data used to generate the structures, IR spectra and proposed frequencies for microwave absorption. In general, the AM1 program is capable of calculating molecular structures, heats of formation, transition state energies and IR spectra. The program also yields force constants between neighboring atoms which are then converted to a vibrational spectrum using normal mode analyses. The frequency of the vibrational transitions are predicted from the calculations that determine the distortion forces necessary to move atom pairs from their equilibrium positions. The intensities of the IR active transitions (oscillator strengths) are also plotted. The calculated spectra represent idealized gas phase spectra and are therefore only an approximation. Certain effects (anharmonic effects, combination transitions, or those forbidden by symmetry) that would have been present in actual spectra of solid or liquid matter are neglected by the program. The calculations are meant to show trends, and shifts in energies or wavelengths. If two identical sets of atoms within a molecule have different vibrational frequencies, then the material, the bond between the two oscillators, or both the bulk material and bond, has been altered.

The program was used to model the behavior of water in both the liquid and vapor form. The ability of water to heat in a 2.45GHz microwave field is well known, but the reasons for this are not well understood. Using the coupled oscillator and quantum MO modeling program, a calculated IR spectra of liquid water was produced. From the IR spectra, a theoretical microwave spectra was calculated (see Figure A-2). Absorption

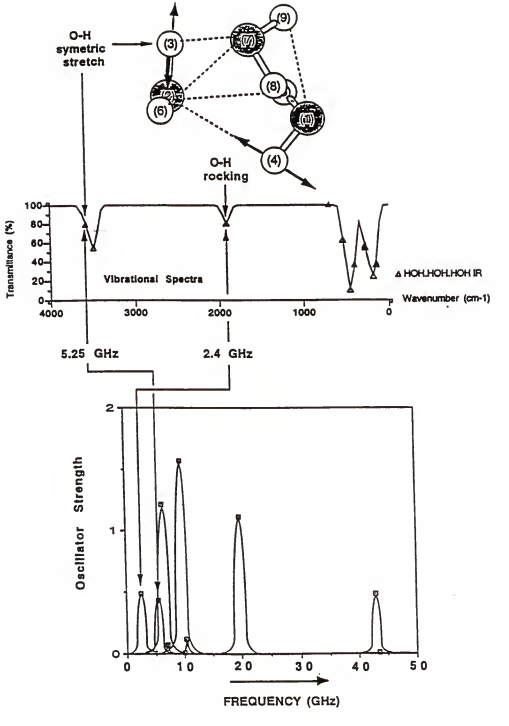


Figure A-2. Molecular structure of liquid water, calculated vibrational and microwave absortion spectra.

features were found at 2.4, 6.15, 9.45, 19.65 and 42.9 GHz [Wes98]. The theoretical data corresponds reasonably well with experimental dielectric data for liquid water as determined by Hasted [Has73]. Though the individual points are so close together that they appear as a single data point, there are 3 coupled oscillators (OH rocking vibrations) located at a frequency of ~ 6 x 10^{13} THz (2000 cm^{-1}) shown in Figure A-2. In theory, all of the atoms or groups of atoms should be oscillating at the same frequency. However, calculated data indicates that this is not the case. The difference between the vibrations corresponds to the energy associated with the transfer of a phonon between the coupled oscillators. The frequency of the phonon is 2.4GHz which is very close to the applied microwave frequency. When the coupled oscillators within the water are exposed to microwave energy, the microwave energy couples with the phonon at a resonant frequency and supplies additional phonons. The addition of phonons acts to increase the amplitude of the vibration (see Figure A-1) and by definition, increases the temperature [Wea86].

Similar calculations for water vapor were carried out. Data indicate little or no absorption at 2.4 GHz (see Figure A-3). Absorption of microwave energy by water vapor does occur within the microwave frequency range (approximately 8, 20, 28, 31, 39 and 70 GHz), but at somewhat reduced oscillator strengths (0.2 -1.0 for water vapor when compared to liquid water 0.5-1.5).

Silicon carbide is often used to aid in heating materials that do not readily react with microwaves and was used in the present study to aid in heating the gases evolved during processing, as well as in the vitrification and metal recovery stages. As anticipated, strong absorption bands are found in the 2.4 GHz region as shown in Figure A-4.

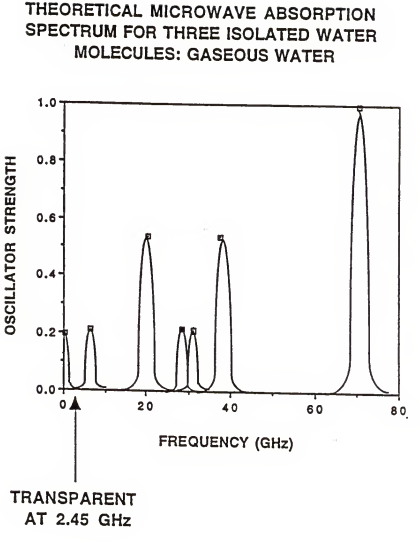


Figure A-3. Calculated microwave absorption spectra for water vapor.

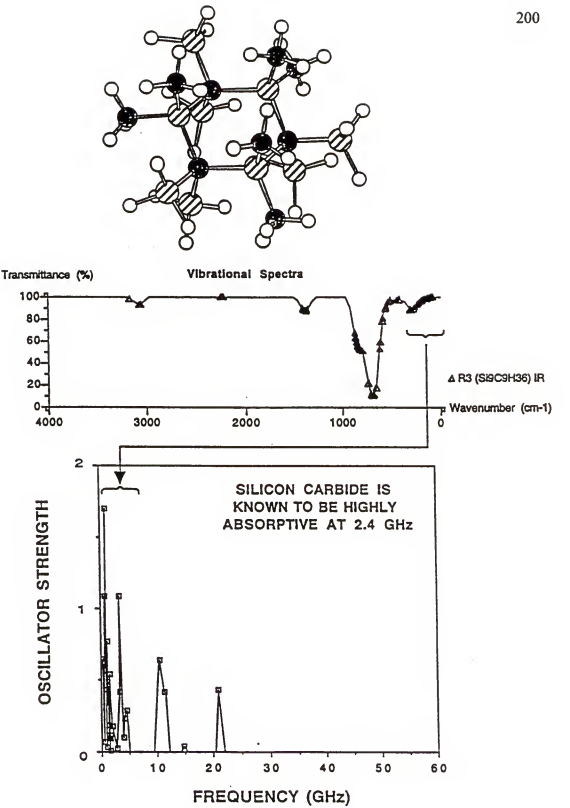


Figure A-4. Molecular structure of silicon carbide, calculated vibrational and microwave absorption spectra.

West also applied his model to some of the gases produced in this study. Benzene was found in every air sample obtained thus far. A summary of the data generated by the AM1 program is shown in Table A-1. One of the areas on the IR spectra that indicates an absorption in the microwave range occurs in the 800-900 cm^{-1} range This corresponds to the C5-C4-C3 rocking vibration coupled to the C5-C6-C1 rocking vibration as shown in Figure A-5. These two sets of atoms should have identical vibrational wavenumbers, but they are slightly different (647.66, 647.80 see Table A-1):

$$\Delta = \frac{(w_1 - w_2)}{2} \qquad \text{A-1}$$

$$f = \Delta c \qquad \text{A-2}$$

where:

Δ = average difference of the vibrational pairs (cm^{-1})

w_1, w_2 = vibrational pair wavenumbers (cm^{-1})

c = speed of light, 2.998×10^{10}cm/sec

f = frequency (1/sec)

According to the model, absorption bands were predicted at around 2.3 GHz (though with a very small oscillator strength), and at ~ 4, 8 and 10 GHz with the peak at 8GHz exhibiting the largest oscillator strength. If a gaseous sample were subjected to microwave irradiation at this frequency, one would expect a measurable indication in absorption of microwaves, perhaps an increase in temperature or a breakdown of the molecule.

Table A-1. Data Generated Using the Austin-Method 1 (AM1) Program for Gaseous Benzene.

```
========================================
AM1 lea Benzene molecule, Optimize geometry IR spectra
========================================
ID Energy  transitionDipole
                                                    MICROWAVE ABSORPTION
                    (GHz)      Oscil
IR Peak    delta     Freq    Strength Oscil   (GHz)      Stre      Oscil
-------  -------  -------  --------- -----  -------  --------  --------
 371.18      0.2        3    0.0012     1  -48078.6    0.0172        30
 371.38   246.95  3704.25    0.0007     2       1.8    0.0018         7
 618.33    29.33   439.95    0.0025     3       2.1    0.0079         4
 647.66     0.14      2.1    0.0079     4         3    0.0012         1
  647.8    96.94   1454.1    0.0075     5       3.6    0.0012         9
 744.74   146.92   2203.8    0.9051     6      4.05    0.0881        13
 891.66     0.12      1.8    0.0018     7       4.8    0.0027        23
 891.78    97.81  1467.15    0.0021     8      7.95    0.0007        16
 989.59     0.24      3.6    0.0012     9       8.4    0.7517        28
 989.83    22.42    336.3    0.0021    10         9    0.0165        26
1012.25    15.83    237.45   0.0028    11       9.9    0.5349        21
1028.08    117.9   1768.5    0.0035    12     40.65    0.0277        25
1145.98     0.27      4.05   0.0881    13       108     0.022        27
1146.25    32.93   493.95     0.088    14    153.45    0.7515        29
1179.18    42.55   638.25    0.0006    15    237.45    0.0028        11
1221.73     0.53      7.95   0.0007    16     336.3    0.0021        10
1222.26     53.5     802.5    0.0005    17    439.95    0.0025         3
1275.76    53.02    795.3    0.0004    18    493.95     0.088        14
1328.78    37.48    562.2         0    19     562.2         0        19
1366.26   212.24   3183.6    0.0005    20    638.25    0.0006        15
  1578.5     0.66      9.9   0.5349    21     795.3    0.0004        18
1579.16    187.7   2815.5    0.5353    22     802.5    0.0005        17
1766.86     0.32      4.8    0.0027    23    1454.1    0.0075         5
1767.18  1416.76  21251.4     0.001    24   1467.15    0.0021         8
3183.94     2.71    40.65    0.0277    25    1768.5    0.0035        12
3186.65      0.6        9    0.0165    26    2203.8    0.9051         6
3187.25      7.2      108    0.022     27    2815.5    0.5353        22
3194.45     0.56      8.4    0.7517    28    3183.6    0.0005        20
3195.01    10.23   153.45    0.7515    29   3704.25    0.0007         2
3205.24 -3205.24 -48078.6    0.0172    30   21251.4     0.001        24
```

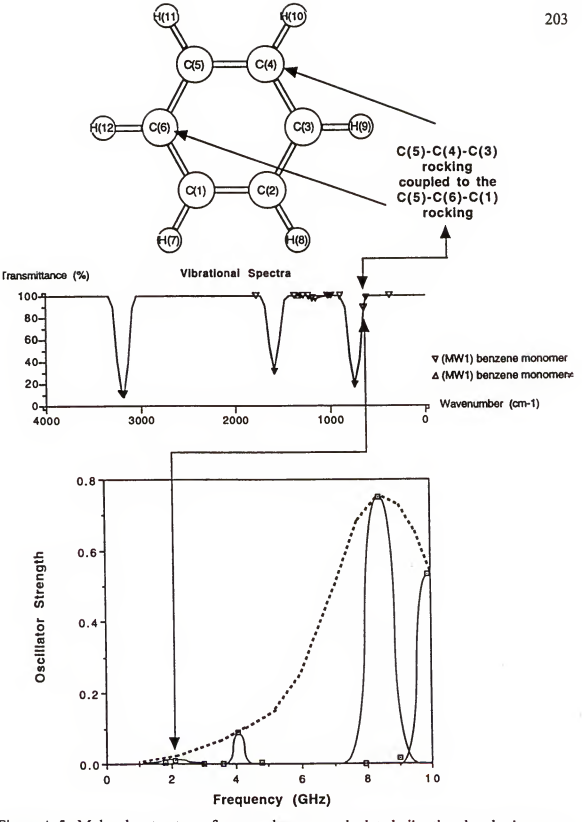


Figure A-5. Molecular structure of gaseous benzene, calculated vibrational and microwave absorption spectra.

Gaseous styrene, also found in most air samples collected thus far, was also modeled using this technique (see Table A-2, Figure A-6). A fairly strong microwave absorption was indicated at 3.6 GHz due to the H2-C8 stretch coupled to the H11-C5 stretch (3182.97, 3183.21cm^{-1}). Other absorption areas are possible, though not shown on the microwave absorption plot.

Data were calculated for liquid toluene where the coupled oscillator was generated by the C19-C19-C17 stretch and the C2-C3-C4 stretch (1640.24 and 1640.09cm^{-1}). This coupled oscillator corresponds to a microwave absorption at approximately 2.25GHz. Other absorption peaks are located at ~1, 3.5, 6.3, 7 and 7.7 GHz. However, for gaseous toluene (Table A-3, Figure A-7), all the coupled oscillator peaks for microwave absorption were far out of the range of what will be the applied frequency of 2.45GHz. From this data, one would assume that liquid toluene would interact with microwave energy, as does water, but not gaseous toluene, as with water vapor.

While the data presented here is preliminary, and experimentation is necessary for verification, it appears the model is a promising method to determine or validate microwave absorption. Also, the model appears to provide a plausible explanation for a mechanism of microwave absorption through the direct absorption of resonance vibrations of coupled oscillators.

The term, "microwave effect," has been a point of discussion and study for microwave researchers for many years [Boo97, Wil97, Wil95, Cla96, Fre93, Fre95, Men95 Kat88]. Those using microwave energy to process various materials and to produce chemical reactions have observed evidence of a microwave effect in the form of lower

Table A-2. Data Generated Using the Austin-Method 1 (AM1) Program For Gaseous Sytrene.

```
=========================================
AM1 lea Styrene molecule, C6H5(CH)CH2, Optimize geometry IR spectra
=========================================
ID Energy  transitionDipole                    MICROWAVE ABSORPTION
                    (GHz)      Oscil
IR Peak     delta    Freq    Strength Oscil    (GHz)      Stre     Oscil
-------  -------  -------  --------- -----  --------  --------  -------
 181.34    78.01  1170.15    0.1269     2  -48255.1    0.5066       42
 259.35   109.59  1643.85    0.0478     3      3.6     0.2076       37
 368.94    61.02   915.3     0.0134     4     18.9     0.0029       12
 429.96    57.45   861.75    0.2943     5     22.2     0.1277        7
 487.41     101     1515     0.0222     6     46.8     0.3751       39
 588.41     1.48    22.2     0.1277     7    66.45     0.111        22
 589.89    67.41  1011.15    0.1199     8     70.8     0.2768       36
  657.3    32.24    483.6     0.0105     9     81.9     0.5089       15
 689.54   120.29  1804.35    0.5061    10    82.35     0.0711       27
 809.83    76.31  1144.65    0.6785    11     87.6     0.1599       38
 886.14     1.26     18.9     0.0029    12   106.95     0.1397       18
  887.4    53.83   807.45    0.0261    13   145.65     0.7164       40
 941.23    40.56    608.4     0.1123    14    220.8     0.0794       21
 981.79     5.46     81.9     0.5089    15   226.95     0.4887       41
 987.25     19.9    298.5     0.1351    16    298.5     0.1351       16
1007.15    36.14    542.1     0.1647    17    315.3     0.0697       32
1043.29     7.13   106.95     0.1397    18    365.4     0.0106       25
1050.42    66.11   991.65    0.6048    19    483.6     0.0105        9
1116.53    62.28    934.2     0.0351    20    542.1     0.1647       17
1178.81    14.72    220.8     0.0794    21    582.6     0.2343       35
1193.53     4.43    66.45      0.111    22    608.4     0.1123       14
1197.96    41.53   622.95    0.0312    23   622.95     0.0312       23
1239.49    65.21   978.15    0.0102    24   807.45     0.0261       13
 1304.7    24.36    365.4     0.0106    25   861.75     0.2943        5
1329.06    60.54    908.1      0.012    26    908.1      0.012       26
 1389.6     5.49    82.35     0.0711    27    915.3     0.0134        4
1395.09    66.01   990.15    0.2183    28    934.2     0.0351       20
 1461.1    106.2     1593     0.2256    29   978.15     0.0102       24
 1567.3    68.01  1020.15    0.5548    30   990.15     0.2183       28
1635.31   124.81  1872.15    0.4801    31   991.65     0.6048       19
1760.12    21.02    315.3     0.0697    32  1011.15     0.1199        8
1781.14    82.67  1240.05    0.1608    33  1020.15     0.5548       30
1863.81   1275.6    19134     0.0096    34  1144.65     0.6785       11
3139.41    38.84    582.6     0.2343    35  1170.15     0.1269        2
3178.25     4.72     70.8     0.2768    36  1240.05     0.1608       33
3182.97     0.24      3.6     0.2076    37     1515     0.0222        6
3183.21     5.84     87.6     0.1599    38     1593     0.2256       29
3189.05     3.12     46.8     0.3751    39  1643.85     0.0478        3
3192.17     9.71   145.65     0.7164    40  1804.35     0.5061       10
3201.88    15.13   226.95     0.4887    41  1872.15     0.4801       31
3217.01 -3217.01 -48255.1     0.5066    42    19134     0.0096       34
```

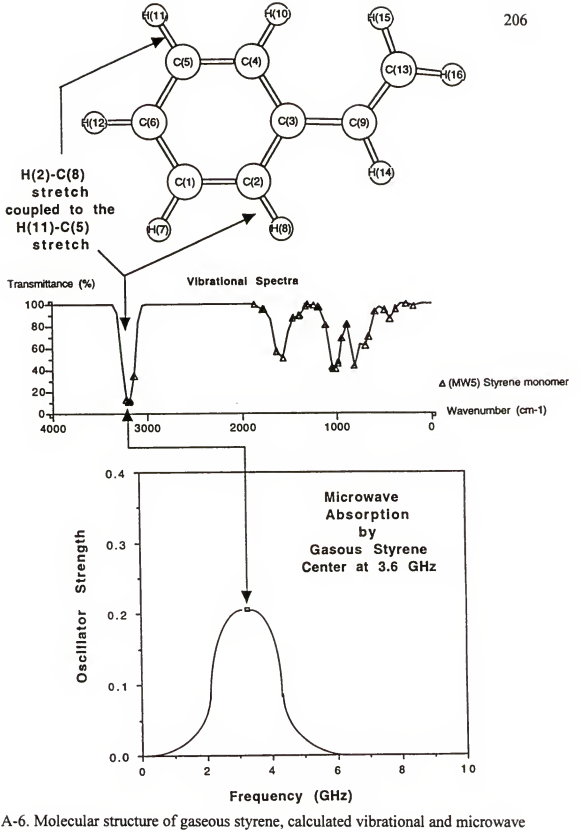
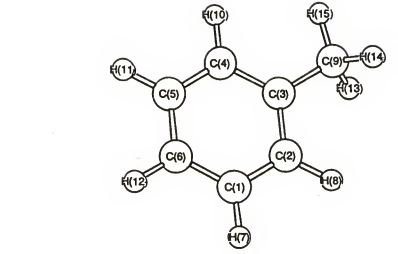


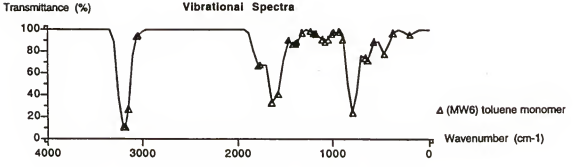
Figure A-6. Molecular structure of gaseous styrene, calculated vibrational and microwave absorption spectra.

Table A-3. Data Generated Using the Austin-Method 1 (AM1) Program For Gaseous Toluene.

```
========================================
AM1 1ea Toluene molecule, C6H5(CH3), Optimize geometry IR spectra
========================================
ID Energy  transitionDipole
```

IR Peak	delta	(GHz) Freq	Oscil Strength	Oscil	MICROWAVE ABSORPTION (GHz)	Stre	Oscil
196.73	170.44	2556.6	0.1467	2	-48040.3	0.391	39
367.17	4.19	62.85	0.072	3	25.5	0.1903	35
371.36	89.17	1337.55	0.0038	4	26.4	0.1303	24
460.53	107.96	1619.4	0.3193	5	45.75	0.4324	37
568.49	67.63	1014.45	0.0837	6	62.85	0.072	3
636.12	22.82	342.3	0.3642	7	71.4	0.1396	36
658.94	129.85	1947.75	0.0274	8	131.4	0.0935	19
788.79	100.55	1508.25	0.757	9	143.4	0.7217	38
889.34	31.65	474.75	0.0016	10	155.4	0.1049	32
920.99	15.58	233.7	0.0487	11	187.5	0.0545	23
936.57	51.67	775.05	0.0802	12	232.05	0.0038	13
988.24	15.47	232.05	0.0038	13	233.7	0.0487	11
1003.71	39.33	589.95	0.0072	14	247.2	0.0815	30
1043.04	34.57	518.55	0.1022	15	286.35	0.0735	18
1077.61	27.68	415.2	0.2001	16	342.3	0.3642	7
1105.29	64.88	973.2	0.0324	17	409.35	0.126	25
1170.17	19.09	286.35	0.0735	18	415.2	0.2001	16
1189.26	8.76	131.4	0.0935	19	467.1	0.0363	20
1198.02	31.14	467.1	0.0363	20	474.75	0.0016	10
1229.16	88.45	1326.75	0.009	21	518.55	0.1022	15
1317.61	53.55	803.25	0.027	22	528.15	0.0896	34
1371.16	12.5	187.5	0.0545	23	589.95	0.0072	14
1383.66	1.76	26.4	0.1303	24	746.1	0.1572	26
1385.42	27.29	409.35	0.126	25	775.05	0.0802	12
1412.71	49.74	746.1	0.1572	26	803.25	0.027	22
1462.45	107.94	1619.1	0.1159	27	973.2	0.0324	17
1570.39	69.78	1046.7	0.5151	28	1014.45	0.0837	6
1640.17	125.17	1877.55	0.6139	29	1046.7	0.5151	28
1765.34	16.48	247.2	0.0815	30	1326.75	0.009	21
1781.82	1264.78	18971.7	0.3972	31	1337.55	0.0038	4
3046.6	10.36	155.4	0.1049	32	1371.75	0.1083	33
3056.96	91.45	1371.75	0.1083	33	1508.25	0.757	9
3148.41	35.21	528.15	0.0896	34	1619.1	0.1159	27
3183.62	1.7	25.5	0.1903	35	1619.4	0.3193	5
3185.32	4.76	71.4	0.1396	36	1877.55	0.6139	29
3190.08	3.05	45.75	0.4324	37	1947.75	0.0274	8
3193.13	9.56	143.4	0.7217	38	2556.6	0.1467	2
3202.69	-3202.69	-48040.3	0.391	39	18971.7	0.3972	31





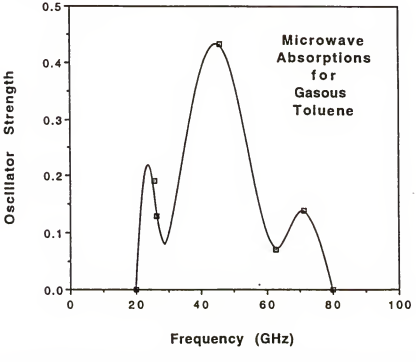


Figure A-7. Molecular structure of gaseous toluene, calculated vibrational and microwave absorption spectra.

processing temperatures, shorter processing times, increased reactivity and better mechanical properties [Cla96]. A microwave effect has been observed for a wide range of materials including ceramics, polymers and even water vapor.

A fairly elegant study was conducted by Vala and Szczepanski [Val97]. In this study, Vala attempted to differentiate between a thermal heating effect and a microwave effect. The methodology selected was to measure the infrared intensities of pairs rotational/vibrational bands of water vapor (both with and without microwave radiation) and then to compare the effective temperatures. Using basic principles of thermodynamics, Vala speculated that since by definition a thermally heated system is at equilibrium, the ratios of the IR bands should indicate the same effective temperature, providing that the only effect microwave irradiation has on the water vapor is heating. If there is a real microwave effect, then the effective temperatures should not be equal.

To verify the supposition, a microwave generator (10-100W, 2.45GHz) was connected to a quartz sample cell via a coaxial cavity positioned within a Fourier transform infrared spectrometer. Temperature was measured using a copper/constantan thermocouple situated outside of the microwave cavity. The OH-stretching mode of water at 3800cm^{-1} was monitored. Spectra were collected at 300K and 360K with the microwave source turned off and the effect on the population of the rotational levels was measured. No differences were observed for the two temperatures. The experiment was repeated with the microwave source activated. When the IR spectra were analyzed, a shift of approximately 0.4-0.9cm^{-1} in the rotational/vibrational band to a lower energy level was observed when compared to the spectra collected when the microwave energy was not activated. Effective temperatures

were derived by calculating the intensity ratio for 2 pairs of rotational/vibrational bands (Band A in the 3_{-2} state and Band B in the 2_0 state) and inserting the ratio values into Boltzman's equation [Val97]:

$$T = \left[\frac{-\Delta E(3_{-2},2_0)}{k}\right] \left[\ln(I_A/1.41I_B)\right]^{-1} \qquad \text{A-3}$$

where:

$\Delta E\ (3_{-2}, 2_0)$ = energy gap (= 47.1cm^{-1} for this case)

I_A/I_B = calculated intensity ratio

k = Boltzman's constant = 1.3807 x 10^{-23} JK^{-1}

an effective temperature of 344.7K was determined. Similar calculations for the C,B and B,D band pairs revealed effective temperatures of 148.9K and 213.9K, respectively. Three different temperatures were determined from the data, leading to the conclusion that the system is not in thermal equilibrium. This tends to support the premise of a microwave effect. While the model proposed by West indicates no microwave absorption at 2.45GHz, the data illustrated in Figure A-2 shows peaks in close proximity on both sides of this frequency. Some microwave absorption in the tail portion of these peaks in the 2.45GHz frequency range maybe responsible for the effects observed by Vala. Discrepencies exist, therefore, an acceptable explanation for these "effects" has yet to be provided.

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BIOGRAPHICAL SKETCH

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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